

COLLOID SYMPOSIUM MONOGRAPH

PAPERS PRESENTED AT THE FOURTH NATIONAL
SYMPOSIUM ON COLLOID CHEMISTRY
THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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FOREWORD

The Fourth National Symposium on Colloid Chemistry sponsored by the Committee on the Chemistry of Colloids of the National Research Council, was held in Cambridge, Massachusetts, June 23, 24, 25, 1926, under the auspices of the Massachusetts Institute of Technology in co-operation with the Northeastern Section of the American Chemical Society. Professor James W. McBain of the University of Bristol was the foreign guest of honor. His valued paper, which appears in this volume, and his scholarly discussions of a number of papers contributed in a large way to the success of the Meeting.

The Fifth Symposium to be held at the University of Michigan in June, 1927, will be sponsored by the Division of Colloid Chemistry of the American Chemical Society, and the proceedings will be published as volume V of the Colloid Symposium Monograph.

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The Rice Institute,
Houston, Texas.

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COLLOID SYMPOSIUM MONOGRAPH

A SURVEY OF THE MAIN PRINCIPLES OF COLLOID SCIENCE

By JAMES W. MCBAIN

Some temerity is required in attempting to pass in review the outstanding generalizations in the subject of colloids. This field of science has so many aspects and is so evidently emerging from the preconceptions adopted twenty years ago that the perspective must necessarily be somewhat individual. Nevertheless the attempt should be justified by its usefulness in calling attention to main principles and in its provocation to further experimental and theoretical study.¹

The two main problems of colloid science are structure and stability. What is the structure which places matter in this category? Whence do such structures derive such a measure of stability as to constitute nearly all the common materials met with in daily life? The answer to the first question is definitely that in most cases the unit of which colloids are built up is not the mere molecule but a higher organized unit, the particle called by Nægeli the micelle.

The question of stability has not been properly faced. I submit that there is a class of substances whose most stable state is the colloidal condition. They are thermodynamically stable in the strictest sense, in that the colloid state is for them more stable than the crystalline or crystalloidal. Many substances have never even been brought into the crystalloidal state, so that proof is necessarily lacking just because they are too strongly colloidal. Nevertheless there are some intermediate substances where both the colloidal and crystalloidal states are producible at will, because they are almost equally stable. This is the most important result of the study of soaps.² Here we can have perfect true crystals in true reversible equilibrium with a solution in which soap exists partly as colloid and partly as crystalloid. From the standpoint of the strictest thermodynamic criteria they possess an exactly equal degree of stability.

¹ Cf. Thomas, *J. Chem. Education*, **2**, 823 (1925); Kruyt, *Nature*, **111**, 827 (1928).

² Cf. McBain and Taylor, *Z. physik. Chem.*, **76**, 208 (1911).

Under other conditions the colloidal form is more stable and the crystal or the true crystalloidal solution passes spontaneously into the colloidal form, thereby demonstrating the lower free energy of the colloidal state for such cases. We have shown that the phase rule governs the external equilibria of all such phases.³

It is evident that this point of view embraces not only sols but also jellies and gels. If accepted, it is much more heartening than the conception, hitherto universal, that colloids are inherently unstable formations which have been brought by various devices into this state of dispersion and are rather precariously kept there, either on account of slow rate of reaction or through a balance of compensating factors which inhibit alteration.

Von Weimarn has made the most extended study of these thermodynamically unstable colloids and his rules for utilizing degree of supersaturation have enabled him to disperse over three hundred different substances, using sixteen different solvents.⁴ The only reason for the continued existence of such colloids is that their surface is homologated to the nature of the solvent, generally by a stabilizing agent, which we shall discuss later.

In dealing with the proposed class of thermodynamically stable colloids, I would further suggest that they can only then be truly stable when the micelle has such a structure that part of every molecule of the micelle is exposed to the solvent. This idea can be best developed by illustration. For example if water and palmitic acid are sealed up in an evacuated tube the most stable and therefore permanent state is that where the palmitic acid forms a monomolecular film upon the surface of the water, any excess remaining as a crystal or crystals.

In the case of soaps there are two kinds of micelle, the neutral and the ionic micelle. The first, following a somewhat modified suggestion of S. E. Sheppard, may be likened to a part of brushes stuck to each other by placing the bristles in contact. Each bristle represents a paraffin chain, so that all the parallel bristles together resemble a solid block of paraffin the length of two molecules in thickness. The backs of the two brushes form the exterior of the neutral micelle and they alone are in contact with the solvent; they comprize the carboxyl group and the sodium or potassium, any electrical double layer, and the water of hydration. Hence the whole exterior is closely similar to a molecule which is soluble such as formic acid or sodium formate.

The ionic micelle may be pictured in terms derived from an old conception of Reychler (1913) recently revived by N. K. Adam, as

³ McBain and Elford, *J. Chem. Soc.*, 129, 421 (1926).

⁴ Von Weimarn, "Die Allgemeinheit des Kolloidzustandes," 2nd Ed. Theodor Steinkopff, 1926.

a ball composed of say ten soap ions, the paraffin chain radiating from the center, the outside being composed of ionized carboxyl groups together with water of hydration. Here again, as the radius of the ball is the length of the soap ion, each ion has its soluble end exposed to the solvent.

Similar structures must be postulated for other truly stable colloids. The finest work in this field is that of O. L. Sponsler⁶ and W. H. Dore on cellulose. Their structural model, to be exhibited at this symposium, is derived from X-ray evidence, and a full description is given in this Monograph. The model accounts for all twenty of the spacings as determined by X-rays. Here there is a question as to whether or not the micelle appears as a filament or more probably a sheet only a few Angstrom units thick, but perhaps extending the whole length of the fiber.

I. Micellar Structures.

Some colloidal particles such as those of gold in water have been shown by X-ray investigation to be actual crystals. This however does not account for their existence in this unstable condition. It is not the nature of the interior but the composition of the exterior of the particle that determines its chief properties and degree of stability. Probably in every case the exterior has to consist of a stabilizing agent. The motto of the colloid is, "Save the surface, and you save all." Even an incomplete monomolecular layer of any suitable soluble material may be sufficient.

1. Individual micelles were assumed by Einstein in 1905 to be equivalent to single molecules from the standpoint of the kinetic theory. This has led to much brilliant work upon the Brownian movement, which has fully substantiated this point of view.⁶ Only in one respect is there an important outstanding discrepancy, which has been the subject of debate in previous Symposia. This is the fact that the expected sedimentation under the influence of gravity is observed only within a very thin layer at the top of the colloidal solution, whereas the bulk of the solution is uniform.⁷ Various forces have been tentatively suggested to account for this but without success. For example, Porter has shown that the Helmholtz double layer would result in an attraction rather than a repulsion between particles. I therefore put forward the point of view (discussed more fully under III below) that the particles behave like large ions and that the

⁶ *J. Gen. Physiol.*, **9**, 221 (1925).

⁷ *Westgren, Z. anorg. Chem.*, **92**, 240 (1915).

⁸ *Burton, Proc. Roy. Soc.*, **100A**, 414 (1922); and especially Porter and Hodges, *Trans Faraday Soc.*, **18**, 1 (1922).

free ions of opposite charge have been forgotten in the discussion. The particles themselves would soon sediment but that would develop large electrostatic attraction between them and the freely diffusible ions of opposite charge which would oppose appreciable separation. The case is somewhat similar to the electrical forces governing the diffusion of ions in considering the diffusion potential between two salt solutions.

The effect of gravity is thus a compromise and is observed only in a vertical direction, and not sideways. At the very top of the solution the heavy particles will hang below the diffusible ions. In the body of the solution a uniform distribution is attained, and at the bottom the elastic rebounds from the bottom of the vessel eliminate further sedimentation.⁸

This suggestion would account for the sedimentation being observed only at the top surface, and would partly explain why colloids should appear least stable at the isoelectric point. Further, emulsions, which in general consist of charged droplets, should not cream if the droplets are made fine enough; whereas very large particles or particles subjected to great force, as in a centrifuge, should sediment.

2. Simple primary micelles existing independently, such as we have been discussing, appear to be quite rare and exceptional. Usually they are more or less loosely aggregated to give larger formations as is frequently pointed out by almost all the well known writers on the subject of colloids when discussing particular cases. I have emphasized⁹ the enormous effect this must have upon the apparent viscosity of the solution. The increase in apparent viscosity is often of a much higher order of magnitude than that calculated by Einstein (or Hatschek) for individual particles (relative viscosity = $1 + 2.5 v$, where v is the fraction of the total volume occupied by the particles), and far transcends that due to true hydration of the particles.

Kruyt and others have recently extended the so-called electroviscous effect predicted by von Smoluchowski¹⁰ from certain poorly conducting systems to other systems about which he explicitly stated his doubts. There seems to be no reason why such an effect should not occur, but its correct quantitative formulation is now in doubt, and it is probably unimportant. For example in a recent paper by Kruyt and Tendeloo¹¹ data are given for aqueous solutions of starch in which the enhancement of the apparent viscosity due to "hydration" (treated as *aggregation* in our preceding paragraph) is calculated to

⁸ It must be remembered that Brownian movement as such does not affect rate of fall and is not responsible for the failure to sediment, since Brownian movement is wholly random and disordered whilst gravity is constant and directed; in a bottomless vessel the rate of fall would on the average be constant forever. An atmosphere owes its existence to the elastic kinetic impacts with the bottom surface.

⁹ McBain, *J. Phys. Chem.*, 30, 239 (1926).

¹⁰ *Kolloid-Z.*, 18, 190 (1916).

¹¹ *Koninklijke Akad. Wetenschappen Amsterdam Proc.*, 27, 877 (1924).

be one hundred times greater than the "electroviscous effect"; thus the latter seems to be relatively of negligible importance.

3. The micellar structure of jellies. In 1916 Hatschek¹³ could write, "The most generally accepted theory of the constitution of coherent gels like gelatin or silicic acid gels is that they consist of two liquid phases." Now as Weiser¹⁴ writes, "The vast majority of investigators incline to the view that jellies are two-phase solid-liquid systems, in which there is a network. . . ." In many cases there is no doubt that the micelles or even the aggregates in the jelly are the same as in the sol from which the jelly was derived, only they are no longer independent but partly stuck to each other in the jelly. Sometimes the aggregates tend to be filamentous. It is interesting that all the typical jellies if carefully enough prepared are transparent and show no visible structure or particles even in the ultramicroscope (unpublished experiments of H. Harris on dibenzoylcystine, barium malonate, lithium urate, etc.).

The relation of jellies to the various types of gels has not yet been worked out. It is rather surprising to find how many cases there are of ready peptization of gels by stabilizing agents—disnmembering of the gel into small aggregates of micelles or into individual micelles by satisfying the respective valencies with adsorbed or combined material. This is peptization in the original sense of Graham.¹⁵ Weiser has explained one aspect of the surface equilibria in insisting that the particles must be hydrous.

Any substance may be produced in the form of a gelatinous precipitate by using von Weimarn's rules involving sufficiently high concentration and sufficiently fine particles. However, true jellies often form in comparatively dilute solution in spite of moderately good solubility. Thus for example true soap jellies under certain conditions may be thermodynamically stable as discussed in the introduction above and form spontaneously from all other less stable states.

4. The structure of gels. Collander's work¹⁶ on the sieve structure of semipermeable membranes of copper ferrocyanide has shown that the interstices between the micelles or aggregates are about 4 Ångstrom units in diameter. I would suggest a still better molecular sieve, namely such crystals as dehydrated zeolites, etc. For example, O. Weigel found that good crystals of chabasite from whose space lattice water has been removed without destroying the space lattice, sorb water, methyl alcohol, ethyl alcohol and formic acid; but will not take up acetone, ether or benzene. From the molecular volumes of these compounds I calculate that the openings in the space lattice

¹³ *Trans. Faraday Soc.*, **12**, 17 (1916).

¹⁴ Bogue's "Colloidal Behaviour," **1**, 378 (1924).

¹⁵ *J. Soc. Chem. Ind.*, **44**, 499T (1925).

¹⁶ *Kolloidchem. Beihfte*, **10**, 72 (1924); **20**, 273 (1925).

are just smaller than 5 Ångstrom units, which permits of the prediction of the sorption of other vapors and even gases.

Many gels appear to have an analogous structure; for example partially dehydrated silica gel or copper oxide or manganese dioxide, and charcoal. Activated charcoal may well consist of a conglomerate of incomplete space lattices into which the sorbed material penetrates. This would render intelligible the time required, the absolute amounts at various periods of time, the relative amounts of various sorbed materials, and some of the phenomena of catalysis. Somewhat similar structures arise when gels are swollen in a suitable liquid and then hardened by a second agent. In many cases it has to be remembered that there is competition for any particular valency of a micelle between the material to be sorbed and other particles; the extent of dismemberment, or conversely, aggregation¹⁶ depends upon the result.

II. Stability.

We have seen that stability whether artificial or inherent is due to the nature of the surface of the micelle. Reactions with a surface are classified as sorption, and sorption embraces all the reactions of colloids. Adsorption often precedes chemical action (and arises from unactivated molecules). It may be due to various forces, residual affinity or stray fields of force, primary valency or shared electrons, or electrostatic form, etc. Reference should be made to the recent summary by H. S. Taylor for the Committee on Contact Catalysis.¹⁷

1. The fundamental theorem is the Gibbs theorem, to which there can be no exception. However, the Gibbs equation correctly takes into account the adsorption of all constituents actually present, whereas in practice as usually applied some constituents are ignored. Secondly, the Gibbs theorem deals with thermodynamic potential, partial molal free energy or activity, whereas it is usually misquoted and misapplied in terms of concentration. Thirdly, only in the rarest cases is the surface tension actually known.

2. The dominant conception is now that of oriented and polar groups. This has been invoked in the introduction to explain not only how the exterior of a micelle may be stabilized but also to explain the structure and hence the existence of the interior of stable micelles. An excellent illustration is that studied by Giles and Salmon,¹⁸ the nonconducting sol of silver in stearic acid where the micelles consist of silver with the essential coating of silver stearate, silver to silver and stearate radical to stearic acid solvent. This same

¹⁶ *Z. Kristallographie*, 61, 125 (1924).

¹⁷ *J. Phys. Chem.*, 30, 145 (1926).

¹⁸ *J. Chem. Soc., London*, 123, 1597 (1923).

conception applied to long molecules explains the close relation between colloids and colloidal electrolytes and liquid crystals.

3. Solvation. Solvation appears to be universal, and the chief function of all stabilizing agents in homologating the surface of the micelle to the solvent is in inducing solvation. Desolvation causes aggregation, coagulation, etc.

4. The Helmholtz electrical double layer probably enfolds many colloidal particles, but its chief function is presumably in stabilizing the colloidal particles through induced solvation. As Porter (*loc. cit.*) has indicated, the Helmholtz double layer as such would rather produce a mutual attraction and therefore coalescence of particles than produce apparent stability through repulsion. Further, the Helmholtz double layer appears to have almost no connection with electrokinetic phenomena¹⁹ such as movement in an electric field (electrophoresis, electro-osmosis, etc.). The modification proposed by Gouy is likewise inadequate²⁰ to connect the double layer satisfactorily with the observed electrokinetic phenomena.

Silicic acid and globulin and other colloids are said to be most stable at the isoelectric point where they show no movement whatever in the electric field. Possibly here the Helmholtz double layer is complete over the whole of their surface, which would account for their stability owing to induced solvation.

For about fifteen years a formulation of "contact potential" between micelle and solvent has been in current use, and even though Hückel has recently introduced a fifty per cent correction for the simplest case the general theoretical treatment, in spite of Helmholtz's great paper, has become wholly unsatisfactory and misleading. The orthodox formulæ which assume movement within the double layer are based upon premises now shown to be invalid. Thus it is assumed that the surface is shielded from all contact with the outer solvent by a complete sheath of ions; the thickness of the whole double layer is assumed to be uniform, all ions or charges of the double layer moving at the same speed; and finally, it is assumed that the film within the double layer is thick enough to exhibit the viscosity and dielectric constant of pure water, although the voltages consistent with this are inadmissibly great.

Freundlich has done good service in emphasizing that the "electrode potential" of a micelle and its "electrokinetic potential" are not necessarily even of the same sign.²¹ However, even this does not go far enough. Consideration of the equilibrium involved in the adsorption of ions and of the dissociation of surface molecules, etc., shows clearly that different parts of the same surface have different contact po-

¹⁹ McBain, *J. Phys. Chem.*, **28**, 708 (1924).

²⁰ Usher, *Trans. Faraday Soc.*, **21**, 406 (1925).

²¹ Freundlich, *National Colloid Symposium*, **3**, 7 (1925).

tentials, and the different parts may differ even in sign. The formulation of the electrokinetic potential therefore needs complete revision.

5. Most colloids resemble electrolytes. The Helmholtz double layer may not be complete, it may even be lacking or much more complicated,²² but if for whatever reason there is on one particle an excess of charges of either sign, the micelle or aggregate will behave as a large ion. The extreme case is the ionic micelle of soap where there is a negative charge for each fatty molecule, or rather ion, in the micelle.

It is a remarkable and unexplained fact that all these particles exhibit a rate of movement in the electric field which is of the same order of magnitude for true ions.

Miss Laing²³ has formulated the theory of this subject and shown by direct experiment that electrophoresis, electro-osmosis, electrolytic migration, etc., are all inherently identical phenomena. The fraction of the current carried by any charged body whether ion or colloid or wall or bubble is equal to the ratio of its actual conductivity to the total conductivity of the system.

$$\text{fraction of current} = \frac{c_1 f_1}{\mu},$$

where c_1 is the concentration and f_1 is the conductivity of unit concentration, and μ is the sum total of all such $c f$ terms for all constituents present.

The bodily movement differs from this by a factor m_1 which is the number of units to one electrical charge,

$$\text{bodily movement} = n_1 = \frac{c_1 m_1 f_1}{\mu}.$$

The factor m_1 may be very large, say many thousands, for ordinary slightly charged colloids, and correspondingly f_1 is exceedingly small. It is $m_1 f_1$ and not f_1 that is comparable with the movements of true ordinary ions u and v whose m is equal to unity; that is, whose charges correspond to their chemical equivalents. Electrophoresis or actual bodily movement is found to be almost independent of the amount of electrical charge, and likewise almost independent of the conductivity of the particles.

Neglect of this factor m_1 is the methodical error which vitiates the recent work of Varga, Wintgen, and Zsigmondy.²⁴ Their "mobilities" have to be divided by m_1 to find the conductivity. They fall into a further error in interpreting U-tube experiments on electrophoresis.

²² Mukherjee, *Phil. Mag.*, (6), 44, 321 (1922).

²³ *J. Phys. Chem.*, 28, 673 (1924).

²⁴ Varga, *Kolloidchem. Beihefte*, 11, 1 (1919); Wintgen, *Z. physik. Chem.*, 103, 238 (1923); 107, 403 (1924); Zsigmondy, "Kolloid-chemie," 5te Aufl., 179-193 (1925).

Both Lash Miller and G. N. Lewis have shown that it is a consequence of the law of the conservation of matter that the "moving boundary" method must give results which are precisely identical with those derived from the Hittorf method of quantitative analysis. These errors and the neglect of the Donnan equilibrium make their numerical values for the charges of colloids something like ten times too large. In no case hitherto has the absolute charge of a colloidal particle been quantitatively measured.

6. The Donnan distribution law appears to be of universal validity for all solutions containing electrolytes. That is, within all parts of a system in equilibrium, for example, within any colloidal solution, or within the different parts of a jelly, the product of the activities of every pair of monovalent diffusible ions must be constant. Approximately, the ionic product in terms of concentration should be constant throughout. Any change subject to a spatial constraint will cause a corresponding redistribution of all other ions in the neighborhood, but the ionic product for each pair of free ions is constant. There is no need of a membrane, as Procter and especially Wilson have shown, to produce the constraint, although the distribution may be highly local and the constancy merely statistical.

While therefore the Donnan distribution occurs wherever several diffusible ions are present, there is serious doubt about the numerical value of the so-called osmotic pressures (really differential pressures against solution of electrolytes) which have been obtained with colloids so far. The experimental values range from one half to tenfold those predicted. Some doubt also attaches to the "membrane potentials" because the diffusion potentials between solutions of potassium chloride and those containing a nondiffusing colloid ion have not yet been elucidated, so that opinions differ.

Grossly exaggerated claims have been made by Loeb and others²⁵ as to the part the Donnan equilibrium plays in colloidal behavior. Loeb's *ad hoc* definition would exclude most of the phenomena of colloids from that subject. For example the fact of gelatination or of coagulation was referred to the subject of "solubility," not of "colloidal behavior." Even in the effects he observed (his experimental results of course are not here in question) the Donnan distribution is only a factor. Two of the three or four phenomena he studied were effects of electrolytes on swelling and on viscosity. In both fields there are other instances of effects on swelling and on viscosity which exceed his tenfold in magnitude and yet cannot be ascribed to the Donnan equilibrium. For example in the case of soaps, so closely related to Loeb's materials, when the viscosity is increased fifty fold by addition of salt the effect is comparatively enormous and it is in the opposite

²⁵ Thomas, *J. Chem. Education*, 2, 827 (1925).

direction to that predicted by Loeb for salts. The other aspect of Loeb's work, which has been most useful, is his emphasis upon the predominant importance of hydrogen and hydroxyl ions. Few would care to deny chemical action between acids or bases and amino acids or their protein derivatives, but the quantitative formulation is that of sorption,²⁶ and other investigators have shown that sorption of various ions is not negligible.

7. The effects of the Hofmeister or lyotrope (Freundlich) series of ions are too striking to be ignored. They have been observed with too many types of colloids²⁷ and in connection with too many systems not even containing colloids to be attributed to systematic experimental error (Loeb). Many of the salient phenomena of reversible colloids such as coagulation by heat are profoundly affected, and often in different directions in acid and alkaline solutions. Similarly with the coagulation of reversible colloids by electrolytes, or their gelatination, or the swelling of jellies. A remarkable case in point is afforded by Michaelis' observations on the swelling of konyaku²⁸ in various electrolytes. Recent workers who have fulfilled Loeb's injunction to keep the pH of their solutions constant have nevertheless observed these effects and found that sorption of these ions occurs and is specific.

III. The Theory of Sparse Surface Dissociation.

Jordis, Lottermoser and Duclaux long ago emphasized that the stabilizing agents in ordinary colloids are ionizable electrolytes. More recently many investigators using very different lines of approach have been led to a common conception of the equilibria on the surface of ordinary slightly charged colloids such as "ferric hydroxide" or "arsenic trisulfide." Stability is ascribed to a small amount of stabilizing agent derived by sorption on the surface, and of this small amount only a minute fraction is dissociated. For example, according to Freundlich the stabilizing agent of Oden's sulfur is derived from pentathionic acid. That of gold sols is according to Pauli derived from auric acid, and that of stannic acid according to Zsigmondy is derived from potassium stannate. It will be seen that these colloidal particles differ greatly from the ionic micelle of such a colloidal electrolyte as soap, and much more nearly resemble that neutral micelle of soap; but with one fundamental difference, that the ordinary colloidal particles are stabilized only through a surface covering. Attention is thus focussed upon the nature of the surface, not of the substratum or interior of the micelle, which is almost a matter of indifference except for its affinity for the

²⁶ Rinde, *Phil. Mag.* (7) 1, 32 (1926).

²⁷ Cf. Hatschek, "Introduction to the Physics and Chemistry of Colloids," 4th edition, 84 (1922).

²⁸ Michaelis, "The Effects of Ions on Colloidal Systems," 93 (1925).

stabilizing agent. The micelle behaves like a chemical individual or large ion which though polyvalent carries many hundreds or thousands of equivalents to each free charge. The reactions are those of these unbalanced ions weighted with the remainder of the particle and therefore less soluble than in the free condition. However, even the unionized molecules of stabilizing agent can exchange radicals with other electrolytes.

A verbal confusion must be referred to here. So far in this paper the word micelle has been used in the sense for which Nägeli originally coined it to denote the colloidal particle. Shortly before the revival of the micellar theory of Nägeli, Duclaux adopted a suggestion of Cotton and Mouton to substitute the word "*la granule*" for Nägeli's "*micelle*," and to call "*la granule*" plus an equivalent amount of opposing free ions "*la micelle*." The word "*micelle*" is now currently used in both senses. For example, it is equally correct to state that the ionic micelle of soap contains no sodium or potassium as to say that this "*micelle*" contains one atom of sodium or potassium for every fatty radicle. The term "*ionic micelle*" has always been used in the original or Nägeli sense. I would continue to preserve the term ionic micelle for the fully charged particle carrying one charge for each equivalent of fatty radicle, whereas the charge on the ordinary "*granule*" or charged particle of such a colloid as gold is perhaps a thousand times less in proportion.

The modern theory of sparse surface dissociation²⁰ lays emphasis upon the chemical side, and does not so often invoke "change in degree of dispersion." For example, it has to explain:

1. The mutual interactions of colloids which are essentially the interaction of the two stabilizing agents:

(a) Sensitization²⁰ when a small amount of a second colloid whether lyophile or lyophobic, and sometimes even of the same sign, is added. (This appears to be particularly important in biology and medicine.)

(b) Mutual coagulation when the two stabilizing agents are equivalent, or destroy each other.

(c) Protective action when a lyophile colloid is in sufficient excess (this is perhaps the most important single application of colloid science).

2. The action of strongly sorbed non-electrolytes in displacing stabilizing agents; or of non-electrolytes in reducing solubility as shown by Thomas and Miss Johnson.

²⁰ Usher, *Trans. Faraday Soc.* (1926); Thomas, *J. Chem. Education*, 2, 383 (1925); also numerous papers since 1917 by Pauli.

²¹ Freundlich, Bogue's, "*Colloidal Behaviour*," 1, 297 (1924).

3. The effect of mere concentration in causing flocculation and the similar effect of added common ion; also the effects of dilution on the coagulation values.

4. The effects of electrolytes in exchange of ions and in consequent increase or decrease of dissociation.

5. The effects of the valency of added ions, and the deviations from the usual rules due to insolubility of the product in special cases.

6. All the electrokinetic behavior on the one hand, as well as capillarity and electrocapillarity on the other.

7. The various "contact potentials" of the same colloidal particle, if indeed contact potential is really a useful conception. In addition to those mentioned already which may vary in origin, magnitude, nature, and even sign for different portions of the same particle, Wilson's discussion of the Donnan equilibrium leads to yet another which scarcely affects the electrokinetic behavior.³¹

In concluding this necessarily personal review of the outstanding principles and generalizations of colloid science, with its attempt to offer a few new suggestions, I would take the opportunity of uttering a plea that the phenomena of colloidal behavior should be described in terms of the directly observed facts rather than of theories or inferences.

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³¹ Usher, *Trans. Faraday Soc.* (1926).

THE COLLOID PARTICLE AS REVEALED BY CATALYTIC STUDIES

BY HUGH S. TAYLOR

A considerable body of evidence is now available¹ with reference to the properties of a catalytic surface, showing that such a surface is not uniformly active and that chemical reactions occur over portions of the surface which may vary in extent from a very small fraction of the surface to the whole area. A theory which takes account of these facts was recently put forward by the writer. For reactions in which only a relatively small fraction of the surface² is catalytically active, the activity is associated with occasional groups of atoms fixed in metastable positions, associated with high energy and chemical unsaturation relative to the atoms in the regular lattice of the crystal granule. The properties of the contact agent are to be differentiated from the bulk properties of the substance of which the catalyst is composed; it is rather the properties of the individual atoms or molecules of the catalyst with the changes in these properties induced by position and arrangement in the catalyst particle, which are of importance in catalytic change. Colloid chemistry is concerned with all such properties of atoms and molecules determined by position and configuration and it is thus that catalytic action may be regarded as a branch of colloid chemistry. Whereas, however, the properties of such atoms and molecules are themselves a sufficient object of colloid study, these surface units are of importance in catalysis only in so far as they affect reactants coming into contact with them.

The object of the present communication is to re-examine the properties of the surface as revealed by catalytic study, in order the better to emphasize colloid chemical problems which they illuminate, rather than to elucidate what, in the last analysis, must be the central problem of the study of contact catalysis, namely, the nature of the activation induced in the *reactants* by association with the activating centers of the surface. This latter problem will be dealt with in detail elsewhere, and in this place only to the extent that it suggests new points of view and new problems to the colloid chemist.

In the development of the theory of the catalytic surface, the writer has already pointed out that activity due to position and arrangement

¹ 3rd and 4th Reports, Committee on Contact Catalysis, *J. Phys. Chem.*, **28**, 898 (1924); **30**, 145 (1926). Constable, *Proc. Roy. Soc.*, **110 A**, 283 (1926).

² *Loc. cit.*, 4th Report.

of atoms requires, as a consequence, that matter in the finely divided condition shall have properties divergent from those of coarsely crystalline material or of atoms in the plane surface of a crystal. A greater solubility of finely divided materials, a higher heat of reaction with a given reagent, a lesser heat of vaporization, abnormal electrode potentials, abnormally high dissociation pressures of molecular species, perhaps, also, a higher velocity of reaction with various reagents, and even a shift of equilibrium may be anticipated.

The greater solubility of finely divided particles is well-known. On the present basis of interpretation it arises from a greater proportion of corners, edges, isolated atoms or ions in the fine as opposed to the coarse material. The greater attractive forces operative at corners and edges revealed in studies of condensation of solid mercury from the vapor³ suggests, also, greater attractive forces between solid and solvent at such positions in the crystal and, hence, the observed higher solubility. Since the closeness of packing of atoms in the crystal face also influences the strength of the attractive forces in those faces—a phenomenon demonstrable by preferential adsorption on certain faces⁴—one might also expect to find a different solubility of different crystal faces. This has been often suggested⁵ but as often denied, quite recently by Valetton.⁶ Differences between the solubilities of the various faces ought to be most marked in those cases where preferential adsorption is most readily demonstrable. Further experiment might reveal such differences. It should also be manifest with crystals whose habit is the formation of plates since this indicates growth in two dimensions greatly in excess of that in the third dimension.

The recent experiments of Dundon and Mack⁷ on the increased solubility of fine calcium sulfate dihydrate, first studied by Hulett,⁸ lead to the conclusion that a part of the enhanced solubility is due to a dehydration consequent on grinding, the anhydrous calcium sulfate having a higher solubility than the dihydrate,⁹ the anhydrous salt at 25° C. being the unstable phase. The ease with which water is lost from such crystals suggests that differences in dissociation pressures of finely divided and coarse crystals of the dihydrate might be demonstrable. The cause of the loss of water on grinding is also of interest. Dundon and Mack show that the dihydrate loses water on grinding in an atmosphere saturated with water vapor at 25° C. This corresponds to a dissociation pressure greater than 23 mm. The dissociation pres-

³ Volmer and Emmermann, *Z. Physik*, 5, 31, 188 (1921); 7, 1 (1921); *Z. physik. Chem.*, 103, 267 (1922).

⁴ Marc and co-workers, *Z. physik. Chem.*, 81, 385 (1908); 87, 470 (1909); 88, 104 (1909); 73, 685 (1910).

⁵ Curie, *Bull. Soc. min. de France*, 8, 145 (1885).

⁶ *Physik. Z.*, 21, 606 (1920).

⁷ *J. Am. Chem. Soc.*, 45, 2479 (1925).

⁸ *Z. physik. Chem.*, 37, 885 (1901); 47, 857 (1904).

⁹ Hillebrand, *J. Am. Chem. Soc.*, 30, 1120 (1908).

sure of the system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ is recorded in Landolt Bornstein's Tables as 9.1 mm. at 25°C ., but rising very steeply with temperature so that the loss might possibly be due entirely to a temperature effect in grinding.

A higher heat of solution of finely divided particles is a consequence of the higher solubility in the case of salts of low solubility where the solubility may, with sufficient accuracy, be assumed to be proportional to the heat of solution. There do not appear to be any direct experimental determinations of this increased heat of solution, but two examples of increased heat of reaction of fine particles are known to the writer. Bäckström, in some unpublished calorimetric work, has shown that finely ground Iceland spar has a higher heat of reaction than the coarsely crystalline material. Ray found¹⁰ a similar effect with finely ground quartz when dissolved in hydrofluoric acid. The same cause may be responsible for the consistently higher heat of combustion of charcoal as opposed to graphite. The abnormally high value of 224,000 calories found for the interaction of oxygen at very low pressures and high temperatures with charcoal,¹¹ as compared with the normal heat of combustion of 94,000-97,000 calories has also been cited in this regard. Attention should be directed to the fact that this very abnormal result with carbon cannot be expected to be often paralleled with other reactions. The large divergence arises from the abnormal stability of the C-C linkage involving a very considerable heat absorption. The heat of oxidation of isolated copper atoms to form copper oxide could not be expected to differ from the normal accepted value for bulk copper by as much as the heat of vaporization of copper, which is of the order of 60,000 calories. A promising field for investigations of abnormal thermal magnitudes is probably with promoted catalysts since, as recent studies have shown,¹² one function of the promoter is to decrease the size of the crystal aggregates.

The thermal sensitivity of metal catalysts, the marked loss of catalytic activity and of adsorptive capacity on heating, the disproportionately large decrease in adsorptive capacity of the more difficultly adsorbed gases are all contributory lines of evidence to the view that in a catalyst surface there are atoms more loosely bound than the normal surface atoms of a crystal. Such atoms should have lesser heats of vaporization than normal surface atoms. There is, as yet, no direct experimental evidence in this direction. The beautiful experiments of Knudsen,¹³ Wood,¹⁴ Langmuir¹⁵ and Volmer and

¹⁰ *Proc. Roy. Soc.*, 101A, 509 (1922).

¹¹ Garner and Blench, *J. Chem. Soc.*, 125, 1288 (1924).

¹² Wyckoff and Crittenden, *J. Am. Chem. Soc.*, 47, 2866 (1925).

¹³ *Ann. Phys.*, 50, 472 (1916).

¹⁴ *Phil. Mag.*, 32, 865 (1916).

¹⁵ *Phys. Rev.*, 8, 149 (1916).

Estermann,¹⁶ on the condensation of metallic films on clear glass surfaces from unidirectional atomic streams of the gaseous metals, enable one, however, to obtain some evidence confirmatory of the view deduced from catalytic studies. The condensation experiments show that there is a critical temperature above which re-evaporation of the condensing atoms from the glass is so rapid that there is not time for other atoms to be condensed alongside to an extent sufficient to form a film which grows. The critical temperature will naturally vary with the metal gas pressure or the intensity of the atom stream and its temperature. Estermann¹⁷ has recently investigated these two influences and has found that the critical temperature of the receiving glass surface, in the case of cadmium and glass, can be varied between -50° and -110° C., by variation in the concentration of the gas stream but not by varying its temperature. The critical temperature is naturally also dependent on the nature of the surface on which condensation occurs; it is lower for glass than for silver in the case of cadmium. For the critical temperature, the vapor pressure of the film of metal may be substituted and measured in its dependence on temperature. In this way Estermann showed that it is about 10^{10} times greater than the vapor pressure of the solid metals at the same temperature. From the dependence on temperature of the vapor pressures of these films, which may also be regarded as adsorptive pressures of the substance on the receiving surface, one can calculate the heats of adsorption or the heats of evaporation of the film layer, using the Clausius equation. Estermann thus calculates a value of 3500 calories per mol for cadmium on glass, 3000 calories per mol for cadmium on copper, 5000 calories per mol for cadmium on silver. These heats of vaporization are approximately $\frac{1}{2}$ to $\frac{1}{4}$ of the heat of vaporization of solid metals ($\text{Cd} = 26,000$ calories per mol), and can undoubtedly be equated to the heat of dissociation of a single atom-atom linkage. The first nuclei in the condensation process are such di-atomic aggregates.¹⁸

The same considerations should apply to compound substances undergoing dissociation. The dissociation pressures of abnormally situated molecules should be high and the consequent thermal data low. I have already indicated two sets of evidence of this kind with manganese dioxide¹⁹ and with mixed oxides.²⁰

The varying electrometric characteristics of electrode materials may also be used as evidence of the influence of particle size on the thermodynamic properties of the particle. Thus, Webb²¹ ascribes

¹⁶ *Z. Physik.*, **7**, 13 (1921).

¹⁷ *Z. Elektrochem.*, **31**, 441 (1925).

¹⁸ See Frenkel *Z. Physik.*, **28**, 117 (1924).

¹⁹ Whitesell and Frazer *J. Am. Chem. Soc.*, **45**, 2841 (1923).

²⁰ Kendall and Fuchs, *ibid.*, **43**, 2017 (1921).

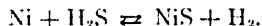
²¹ *J. phys. Chem.*, **29**, 816 (1925).

higher entropies to electrolytic silver chloride and silver iodide as compared with the precipitated varieties and suggests that the very finely crystalline electrolytic variety is a closer approach to the amorphous condition. Cold drawn metals are anodes to annealed electrodes of the same material in a solution of the metal salt. This also is in harmony with the conclusions concerning the influence of fine crystals.

We may anticipate also that in cases where we are dealing with surface atoms of abnormal activity the ordinary equilibrium data may not apply. This seems to have been realized experimentally in one case recently reported by Pease and Cook.²² In studying the equilibrium in the system



attained from both sides, the authors call special attention to "the observations which indicate that excessively high yields of gaseous products are obtained in the early stages of both reduction and oxidation." As the authors point out, "the results are to be expected if the free energies of formation of thin films of oxide on metal and of metal on oxide are higher than those of the oxide and metal, respectively, in the massive state." Now, this is exactly the conclusion which Estermann reaches in the work cited above, since the free energy of the film is directly proportional to its vapor pressure or adsorption pressure on the underlying surface. Expressed otherwise, the free energy of formation of nickel and water is greater for a system of isolated nickel oxide molecules on nickel surfaces than it is for a plane surface of nickel oxide. This point of view also explains the abnormal sensitivity of catalysts to poisons in reactions in which only small fractions of the surface are active. We may illustrate this in connection with the poisoning of active nickel catalysts for hydrogenation processes by small amounts of hydrogen sulfide. The concentrations of hydrogen sulfide which suffice to suppress gaseous hydrogenations, difficultly achieved, are far less than would be calculated as permissible from the equilibrium process

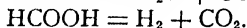
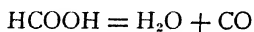


From a knowledge of the permissible upper limit of hydrogen sulfide, the equilibrium constant $p\text{H}_2\text{S}/p\text{H}_2$ thus obtained can be used to deduce the heat of the reaction and hence the heat of formation of the nickel sulfide involved. In this manner the writer and his former student, Dr. J. S. Beckley, demonstrated that the thermal magnitude thus obtained was markedly higher than the accepted value for massive nickel sulfide, a conclusion identical with that of Pease and Cook for the nickel-steam system.

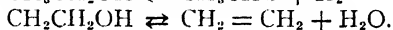
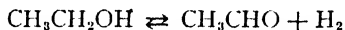
²² *J. Am. Chem. Soc.*, **48**, 1199 (1926).

Mechanism of Activation and the Nature of the Catalytic Surface:

The problem of the mechanism of activation of reactants at a catalytic surface may also be suggestive as to the nature of the catalyst surface. Researches on alternative modes of reaction (e.g., decomposition) of adsorbed reactants indicate that two or more modes of reaction may be secured. Thus, formic acid may decompose to yield carbon monoxide and water or, alternatively, carbon dioxide and hydrogen.



Straight chain alcohols may yield olefine and water or aldehyde and hydrogen.



In a paper to the First National Colloid Symposium I suggested that, in the case of such organic molecules, the nature of the decomposition products must be determined by the nature of the changes in configuration caused by the attachment of the reactant to the catalyst. I illustrated the variation which such attachment might cause by the example of the varying influence of substitution of a $-\text{Cl}$ or $-\text{NH}_2$ grouping on the acidic hydrogen of acetic acid, resulting, respectively, in a weaker and a stronger attachment of the hydrogen ion to the organic anion. I postulated that, dependent on the mode of attachment to the catalyst, the hydrogen atoms in formic acid might be given greater atomic freedom—leading to dehydrogenation—or less freedom and therefore producing a dehydration split. It is now possible to reopen this matter and to give to it a greater precision.

In the Fourth Report of the Committee on Contact Catalysis, I took occasion to point out that there was strong evidence from the data of Adkins and his co-workers that possible contamination of oxide catalysts with alkaline or salt poisons might explain some of the data on alternative decomposition. Alkali poisons seemed to favor dehydrogenation in a titania catalyst essentially dehydrating in characteristics. The converse of this would mean that acidic poisons might alter the characteristics of a dehydrogenation catalyst towards the dehydration side. I also pointed out that Bischoff and Adkins had themselves experimentally demonstrated that both ammonia and water were capable of altering the ratio of dehydration to dehydrogenation products in decompositions of alcohols at titania surfaces. Furthermore, Adkins and Nissen had shown²⁹ that in the decomposition of formic acid the percentage of water in the acid might either increase or decrease the ratio of dehydration to dehydrogenation.

²⁹ *J. Am. Chem. Soc.*, **45**, 811 (1923).

Oxides as Dual Catalysts:

It is significant that, in the case of formic acid decomposition, in presence of metal catalysts the reaction products are exclusively those of dehydrogenation, hydrogen and carbon dioxide, irrespective of the metal. With oxide catalysts, on the other hand, the products may be dehydrogenation as, for example, with zinc oxide, or mainly dehydration as, for example, with aluminium oxide. To what can this variation be attributed. A metal surface is composed of metal ions and electrons, an oxide surface of metal ions and oxide ions. The conclusion seems inevitable that, on the metal ion (positively charged) the dehydrogenation process occurs, whilst on the oxide ion, dehydration occurs. Attachment to the positive ion has the effect of giving the hydrogen atoms in the formic acid molecule greater freedom, in agreement with the observation made above that substitution by an electronegative substituent such as chlorine causes the hydrogen ion to have greater freedom. The negative oxide ion causes the hydrogen atoms to be more firmly attached and so the dehydration split is favored. On this basis, *an oxide catalyst surface is to be regarded as composed, not of a single catalyst, but of two catalysts, metal ions and oxide ions and the nature of the changes induced in the adsorbed reactant is determined by the charge of the ion on which the reactant molecule is adsorbed. The extent of the two alternative changes will be determined by the relative extent of adsorption of reactant on the two ions, on the relative frequency of the two ions in the surface and on their specific individual catalytic activities. These several factors, extent of adsorption, frequency of ions in the surface and catalytic activity will be determined by the degree of saturation of the lattice ions (i.e., catalyst structure) and by the extent to which the ions are already covered by poisons (salts, ammonia, water, etc.).* This conclusion is in good accord with the data of colloid chemistry. It is of inestimable advantage in catalytic study since it permits a forecast of catalytic phenomena. Let us examine firstly the case of salt poisons.

Salt Poisons: The colloid chemist regards a silver halide colloid particle surface as composed of an alternation of silver and halide ions. Adsorption of electrolytes on such a surface is akin to the process of crystal formation. On the silver ions negatively charged ions are adsorbed. On the halide ions, positive ions are adsorbed. The adsorption of ions is frequently unequal so that the particle acquires a charge. Common ions are markedly adsorbed so that in solutions of silver salts the particle becomes positively charged. In solutions containing the halide ion it acquires a negative charge.

Transferring this process to the case of a catalytic oxide, for example, magnesium oxide, we can predict that magnesium sulfate will

be adsorbed. An atomic examination of the surface would now reveal as many magnesium ions as before adsorption, the adsorbed magnesium ions covering an equal number of oxide ions. Covering magnesium ions there will be adsorbed sulfate ions. The net result will be that the surface now contains as many magnesium ions as previously, fewer oxide ions and sulfate ions equivalent in number to the oxide ion decrease. We now have a surface containing three catalytic agents each with its own specific attractive force for the reactant, each with its own specific influence on the adsorbed reactant. Can the result be predicted? It can, for there are available data which demonstrate the efficiency of sulfate ions relative to oxide ions and these are the only variables resulting from the adsorption of magnesium sulfate. Magnesia is listed by Sabatier²⁴ as a 100 per cent dehydrogenation catalyst for alcohols, whereas magnesium sulfate is also cited by the same author²⁵ as an efficient dehydration catalyst for glycerol. The same is true also in the case of zinc. It has been shown by Brus,²⁶ in the decomposition of alcohols at zinc sulfate and zinc oxide surfaces, that the zinc oxide is predominantly a dehydrogenating surface while zinc sulfate although still mainly dehydrogenating is also markedly dehydrating. His experimental figures show that, with ethyl alcohol on the two catalysts at 420° C., the percentage yields of ethylene reaction and of hydrogen reaction are

	Per Cent H ₂ Yield	Per Cent C ₂ H ₄ Yield
(a) Zinc oxide	94	6
(b) Zinc sulfate	85	15

This shows that sulfate ion is more efficiently dehydrating than is oxide ion and this conclusion can be generalized for these two ions irrespective of the cation present in the surface. The prediction can, therefore, be freely made that the presence of sulfate ion, and, for similar reasons, the anions of all the oxy-acids will cause an increase of dehydration ratio in the case of such predominantly dehydrogenation catalysts as uranium oxide, molybdenum oxide, ferric oxide and vanadium oxide.

Alkali Poisons: For oxides which are predominantly dehydrating in their action as, for example, alumina, titania and silica, we may examine the phenomena occurring when an alkali is adsorbed. In a manner similar to the preceding case, adsorption of sodium hydroxide, for example, will decrease the aluminium ions, increase the sodium ions, the oxide ions remaining the same in number or being replaced by hydroxyl ions. The increase of sodium ions has the effect, as the writer

²⁴ Sabatier-Reid, Section 702.

²⁵ Sabatier-Reid, Section 725.

²⁶ *Bull. soc. chim.*, 33, 1438 (1928).

pointed out as evident from the researches of Bischoff and Adkins²⁷ in the case of titania, of converting the reaction from a predominantly dehydrating action to a reaction still markedly dehydrating but also dehydrogenating. From this we conclude that sodium ions are much more pronouncedly dehydrogenating than aluminium ions. This conclusion can also be extended to positive ions of the alkaline earth group since Charriou²⁸ showed that lime inhibited the dehydrating action of alumina.

Dual Oxide Catalysts in Absence of Salt and Alkali Poisons: The concept of an oxide catalyst as consisting of two catalysts enables one to answer a puzzling question raised by Adkins²⁹ in his comments on the proposal of the writer that poisons and unsaturated atoms might suffice to explain the many results which Adkins and his collaborators had obtained. Adkins inquired what caused the differences in catalytic activity of those catalysts that had been prepared by hydrolysis of products that had been repeatedly distilled. The answer, on the present basis, would be that the method of preparation resulted in varying ratios of aluminium and oxide ions in the surface of the catalysts prepared from the several alkoxides. By the laws of chance, this ratio would be constant for several preparations from the same alkoxide with a given method of preparation, but different with a different alkoxide or other raw material as starting point. As already pointed out, the frequency of the ions in the surface will be determined by the catalyst structure and by the extent of covering by poisons. Since, in the case of distilled products, there can be no question of salt poisons the field of poison is, in this case, narrowed down to volatile poisons and, probably, only water and alcohol. The concept differs from that of Adkins in that the ratio of positive and negative ions in the catalyst surface is the important factor, not the atom "spacing."

The concept of two catalyst units in the surface also accounts for the observation as to the influence of concentrations of formic acid on the ratio of reaction products at various alumina surfaces. Adkins and Nissen³⁰ showed that, as the concentration of formic acid was decreased by added water, the influence of the water caused first an increase in the dehydrating ratio and then a very pronounced decrease. Any directional change of a curve showing either a maximum, minimum or point of inflexion (in this case, a maximum dehydrating ratio at 92 per cent, HCOOH) points to the operation of two influences, in this case the competition between water and formic acid for position on the two catalytic agents, aluminium and oxide ions.

²⁷ *J. Am. Chem. Soc.*, **47**, 807 (1925).

²⁸ *Compt. rend.*, **180**, 213 (1925).

²⁹ 4th Report, *loc. cit.*

³⁰ *J. Am. Chem. Soc.*, **45**, 811 (1923).

It is significant, also, that, with a constant formic acid concentration, 92 per cent, the temperature coefficient of dehydration is greater with the catalyst, No. 1, alumina from aluminium amalgam and water which has a greater dehydration ratio at every temperature than that of catalyst, No. 3, for aluminium isopropoxide.

Does the concept help to an explanation of why zinc oxide is predominantly a dehydrogenation catalyst and aluminium oxide, titania, silica, and thorium oxides are equally predominantly dehydration catalysts? It is apparent that, in the latter type, the oxide ions are numerically predominant as opposed to zinc oxide where there are equal numbers of each ion. Professor Bray has suggested that the activity of zinc ions compared with oxide ions is to be associated with the well-known capacity of zinc ion to add to itself, forming complex ions, indicating a stronger adsorptive capacity of the positive ion. Some such assumption would also be necessary to account for the case of chromium oxide which is more pronouncedly dehydrogenating than alumina although the numerical ratio of ions is the same. The characteristics of the individual ions must be, however, the predominant factors, since, with the oxides of uranium and molybdenum dehydrogenation is the predominant characteristic, although the oxide ions are more numerous.

It is very evident that there are problems, and to spare, in the more difficult field of contact catalysis at ionic surfaces. They demand for their solution the thought and co-operation of those interested in the colloid aspects as well as those whose primary interest is the catalytic processes which may thereby be achieved.

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THE WATER EQUILIBRIUM

BY WILDER D. BANCROFT

Gelatine is peptized by potassium iodide solution much more readily than by a potassium chloride solution. It is a typical case of the Hofmeister series. The most obvious explanation is that the iodine ion is adsorbed much more strongly than the chlorine ion, and I have held to that as a working hypothesis for several years. The difficulty with it is that nobody has been able to show marked selective adsorption of iodine ion, as required by the hypothesis. Since potassium iodide is a more effective peptizing agent than potassium chloride both in slightly acid and in slightly alkaline solution, the explanation cannot be right, because there should then be a reversal of effect as one changes from positively charged to negatively charged gelatine or vice-versa.

We cannot be dealing with a solvent action of liquefied potassium iodide because the gelatine is peptized and not dissolved. It cannot be a peptization by liquefied potassium iodide because that would mean a selective adsorption of iodide, which we do not have. We have apparently excluded all direct action of potassium iodide on gelatine, in which case the only remaining possibility is an indirect action of potassium iodide on the gelatine. The potassium iodide may modify the water in such a way as to make the water more able to peptize gelatine at a given temperature. This hypothesis is the more plausible because the Hofmeister series crops up in one form or another in a large number of cases and the water seems to be the only thing in common. It cannot be a question of hydration alone, because the formation of hydrates of potassium iodide in solution would decrease the amount of free water and would therefore decrease and not increase the peptizing or liquefying action of the solution on gelatine.

Liquid water is usually considered to be an associated liquid in which we have equilibrium between hydrol (H_2O) and other forms, say dihydrol ($(H_2O)_2$), trihydrol ($(H_2O)_3$), and polyhydrols ($(H_2O)_n$). For the present it is impossible to differentiate the hydrols to any great extent and I am therefore going to consider water temporarily as consisting of a mixture of a depolymerized form which I will call hydrol and a polymerized form which I will call polyhydrol. We know that the equilibrium between these two forms may be displaced

by the addition of any other component. If the added component is more soluble in polyhydrol than in hydrol, the equilibrium will be displaced to the polyhydrol side. There have been quantitative studies of this sort of thing with NO_2 and N_2O_4 in different solvents¹ and Beckmann² has classified solvents according to their power of polymerizing organic acids.

It is evident that a polymerized form will not necessarily behave exactly like a depolymerized form and that therefore hydrol may have solvent or peptizing powers which are not identical with those of polyhydrol. There is nothing new about this. H. E. Armstrong has blamed the physical chemists for decades because they treated water simply as water and not as a mixture of substances. Sutherland has calculated the amounts and the densities of two forms of liquid water under certain conditions. The orthodox explanation for the temperature of maximum density of water and the displacement of that temperature by the addition of salts is the occurrence of two forms of liquid water and the displacement of the equilibrium between them. In this very case we have a Hofmeister series for chloride, bromide, and iodide, though there seems to be some difficulty about sulfate. Bousfield³ has laid great stress on the effects due to the depolymerization of water, and many other instances could be given.

All I am trying to do is to show, perhaps a little more specifically, the great importance of the water equilibrium for certain problems which are of great interest to the colloid chemist and to the physical chemist. In the particular case of gelatine our hypothesis means that one form of water does not peptize gelatine as readily as the other form, that potassium iodide displaces the water equilibrium so as to produce more of the form which peptizes gelatine readily, and that potassium chloride produces a lesser displacement of equilibrium in the same direction. There is nothing in the general hypothesis to show whether hydrol or polyhydrol peptizes gelatine more readily. Since potassium iodide lowers the temperature of the maximum density of water and since this lowering is believed to be due to increased formation of hydrol, we deduce that addition of potassium iodide causes increased formation of hydrol. If that is the case we ought to get an effect similar to that of potassium iodide by increasing the amount of hydrol in other ways, say by raising the temperature. As we all know, we can liquefy gelatine in hot water. This is of no real value as a proof because it is quite possible that we could have liquefied gelatine in hot water even if there had been no displacement of the water equilibrium.

It will be more interesting to consider a case in which the poly-

¹ Cundall, *J. Chem. Soc.*, 59, 1076 (1891); 67, 794 (1895).

² *Z. physik. Chem.*, 6, 437 (1890).

³ *Trans. Faraday Soc.*, 15, 47 (1919).

merized form of a liquid is the active substance. Pyroxylin is peptized by an ether-alcohol mixture and not by either pure liquid at room temperature. Ethyl alcohol causes pyroxylin to swell appreciably while ethyl ether does not. It has been shown by Lunge⁴ and confirmed by Byron⁵ in the Cornell laboratory that the ether apparently plays no direct part in the peptization of the pyroxylin. It must therefore activate the alcohol by increasing or decreasing the relative amount of depolymerized alcohol. If the depolymerized alcohol is the peptizing agent, it should be possible to peptize pyroxylin by alcohol alone at higher temperatures. If the polymerized alcohol is the peptizing agent, it should be possible to peptize pyroxylin by alcohol alone at lower temperatures. It has been shown by McBain⁶ and confirmed by Byron that there is no appreciable peptization of pyroxylin by alcohol at 140°. It has been shown by Kugelmass⁷ and by McBain, and confirmed by Byron, that pyroxylin is peptized by alcohol at very low temperatures. If the hypothesis is right, a colloidal solution prepared at low temperatures should become more viscous at the temperature rises because the relative amount of the peptizing agent decreases with rising temperature. It has been shown by McBain and confirmed by Byron that a colloidal solution of pyroxylin in alcohol, which is quite mobile at low temperatures, becomes a soft, flowing jelly at room temperatures. It has been shown by Byron that this soft flowing mass becomes a stiff jelly when heated well above 100°, and that the tube can be turned upside down without the contents flowing out.

This is a striking illustration of the effect which may be produced by a polymerization of a liquid and it opens up a number of new problems, not the least interesting of which is to find out why ether increases the degree of polymerization of alcohol. For the present, however, I wish to call attention to certain problems which have troubled physical chemists for a generation. The first of these is the dilution law. I cannot guarantee an explanation of our difficulties; but I can suggest a new line of attack. The constancy of the dissociation constant depends of course on the constancy of the solvent because the dissociation constant is a function of the nature of the solvent. If the water equilibrium is displaced appreciably with increasing concentration of a salt, acid, or base, the dissociation constant will also vary. It is impossible to say that the dilution law will hold for strong electrolytes if we take this factor into account but it is unjustifiable to say that it does not hold until we have taken

⁴ *Z. angew. Chem.*, 14, 588 (1910).

⁵ *J. phys. Chem.*, 30, 1116 (1926).

⁶ McBain, Harvey, and Smith, *J. Phys. Chem.*, 30, 812 (1926).

⁷ *Rec. trav. chim.*, 41, 751 (1922).

this factor into account, and there is very little to be gained by devising empirical formulas which ignore this factor.

There is another case in which I can be more definite. The neutral salt effect has been a source of worry for many years and has given rise to innumerable papers. On adding sodium chloride to a hydrochloric acid solution we should expect a slight forcing back of the dissociation because we are adding a salt with a common ion. What we actually get is an increase in the rate of hydrolysis of the esters and in the apparent hydrogen ion concentration as determined potentiometrically. We have invented ingenious explanations for this neutral salt effect without troubling ourselves to make certain that any actual change of hydrogen ion concentration occurs. The first thing that strikes me is that our different methods of determining hydrogen concentration give us very different results. Akerlof^{*} found that four-normal sodium chloride increased the apparent hydrogen ion concentration of the hydrochloric acid by about five hundred per cent and the rate of inversion by only about one hundred per cent. Preliminary experiments in the Cornell laboratory show a different relation for the inversion of sugar. The freezing-point determinations give a third set of values and the conductivity measurements a fourth.

This makes it probable that there may be errors in some one—and perhaps in all—of our methods of determining hydrogen ion concentrations. Let us consider the potentiometric method first. If we have a cell $H_2|c_1HCl|c_2HCl|H_2$ and we eliminate or correct for the potential difference between the two solutions, the electromotive force as calculated by the Nernst formula will be $E = \frac{RT}{F} \left\{ \log \frac{P}{\alpha_1 c_1} - \log \frac{P}{\alpha_2 c_2} \right\}$ where α_1 and α_2 are the dissociations in the two solutions and consequently $\alpha_1 c_1$ and $\alpha_2 c_2$ are equal to (or proportional to) p_1 and p_2 respectively, the osmotic pressures of the hydrogen ions in the two solutions. If the second solution is so dilute that we may consider the dissociation as complete, and if the solution pressure term, $\log P$, does not change with the concentration, the equation becomes

$$E = \frac{RT}{F} \left\{ \log \frac{P}{\alpha_1 c_1} - \log \frac{P}{c_2} \right\} = \frac{RT}{F} \log \frac{c_2}{\alpha_1 c_1}$$

If we determine E , we can solve for α , and that is the way in which we ordinarily determine hydrogen ion concentrations in principle, though we may actually measure the half-cell against a calomel electrode or against a standard hydrogen electrode, adding or subtracting a suitable constant in each case. If the solution pressure varies with the concentration, however, the equation becomes

^{*} *Z. physik. Chem.*, 98, 260 (1921).

$$E = \frac{RT}{F} \left\{ \log \frac{P_1}{\alpha_1 c_1} - \log \frac{P}{c_2} \right\}$$

and one cannot calculate the value of α_1 because there are three (or two) unknown quantities in the equation.

I am not interested for the moment in the question whether the so-called solution pressure varies enough with the concentration to make all determinations of hydrogen ion concentrations of doubtful value. I am interested in the neutral salt effect because there it is not a question of quibbling over trifles. If we start with 0.1N HCl and add enough sodium chloride to make the apparent hydrogen ion concentration equivalent to 0.5N HCl, which can be done without trouble, we cannot possibly be measuring changes in hydrogen ion concentration alone. No one would consider anything less than 60 per cent dissociation for 0.1N HCl and most people would stand out for at least 85 per cent dissociation. A 300 per cent dissociation or higher is of course absurd and consequently we know that we are measuring something other than the change in hydrogen ion concentration. The other variable is, therefore, $\log P$, the logarithm of the so-called solution pressure.

It may be well to substitute another phrase for the logarithm of the so-called solution pressure. In the case of a strictly reversible electrode we know that the potential difference is equal to the difference of the chemical potentials. The chemical potential of the metal is of course a constant at constant temperature and pressure. We may, therefore, write, if we like

$$\pi = \frac{RT}{nF} \log A.$$

The chemical potential of the ion for which the electrode is reversible is composed of two terms, one for the ion at unit concentration and one for the concentration. We may write

$$\pi_1 = \frac{RT}{nF} \log B + \frac{RT}{nF} \log p_1.$$

The potential difference between the metal and the solution is

$$\pi - \pi_1 = \frac{RT}{nF} (\log A - \log B - \log p_1).$$

If we write E' for $\pi - \pi_1$ and $\log P$ for $\log (A/B)$ we come right back to the Nernst equation

$$E' = \frac{RT}{nF} \log \frac{P}{P_1}.$$

Since $a_i c_i$ is equal to (or proportional to) p_i , one can be substituted for the other. We see, then, that a decrease in E' , the single-potential difference, may be due to an increase in the osmotic pressure (concentration) of the ion, to a decrease in the solution pressure P_1 or to some combination of the two. Instead of a decrease in the solution pressure of hydrogen we may say that we have an increase in the chemical potential of hydrogen ion. The advantage of this is that it enables us to make plausible the relation between the potentiometric data and those on the color changes of the indicators. Few people would admit that the color change of an indicator depends on the solution pressure of hydrogen gas; but few would dare deny that it depends on the chemical potential of hydrogen ion. There is all the difference in the world between tweedledum and tweedledee. With indicators having a large salt error the color change depends also upon another factor which has not yet been determined.

In the case of the hydrolysis of the esters, the change in the solvent will produce an unpredictable change in the reaction velocity which need not stand in any necessary relation to the change in the apparent concentration of hydrogen ion.

The present line of thought causes me to criticize the distinctly formal treatment of equilibrium by means of the activity concept.⁹ "Although we have already seen that the molal free energy makes a very satisfactory quantitative measure of the escaping tendency, there are certain respects in which this function is awkward. For instance, the molal free energy of a gas approaches an infinite negative value as the pressure approaches zero, and we shall see that this kind of inconvenience enters even more in the study of the partial molal free energy in solutions. For such reasons another scale of measurement of the escaping tendency is sometimes to be preferred, and we shall not hesitate to employ, side by side with the molal free energy, a second measure of the escaping tendency, which is called the *fugacity*. . . ."¹⁰

"We may partially define the fugacity f , in terms of the free energy, F , through the equation

$$F = RT \ln f + B,$$

where B is defined no further than by the statement that it is a function of temperature only, or, in other words, that it is a constant at a single temperature."

"If we consider one constituent of a solution at two different concentrations, but at the same temperature, and if by some method we determine for this constituent $\Delta F = F - F'$ between these concentra-

⁹ Lewis and Randall, "Thermodynamics," 190, 191, 254, 328 (1923).

¹⁰ Lewis, *Proc. Am. Acad.*, 37, 49 (1901); *Z. physik. Chem.*, 38, 205 (1901).

tions, then we have also determined the ratio of the fugacities. For, by Equation XVIII-7,

$$F - F' = RT \ln \frac{f}{f'}.$$

"Now we often have occasion to determine and to use such a ratio of fugacities when it is impossible or inexpedient to determine the numerical value of either fugacity; for example, we may be dealing with an almost involatile substance. It has therefore proved advantageous to consider, at a given temperature, the ratio between the fugacity f of a substance in some given state and its fugacity f° in some state which, for temporary convenience, is chosen as a *standard state*. This relative fugacity¹¹ is called the *activity* and denoted by a . Thus in the standard state the activity is unity, $a^\circ = 1$, while in any other state it is given by the equations,

$$a = \frac{f}{f^\circ}; \quad F - F^\circ = RT \ln a$$

where at a given temperature, the molal free energy in any state is F , and in the standard state F° ."

"The mean activity of the ions, a' , divided by the molality of the electrolyte, gives a quantity which has been called the thermodynamic degree of dissociation, since it may be used to replace the degree of dissociation as used in the older formulas. This quantity has also been called the activity coefficient,¹² and, in order to avoid any implication as to the molecular species which may be present, this is the term which we shall ordinarily employ henceforth.¹³ It will be denoted by γ ."

The question of activity is given in a condensed and perhaps more intelligible form by Dawson.¹⁴ "Methods for the determination of the activities of the components of a solution—solute, solvent, molecules, and ions—have been worked out by G. N. Lewis and his collaborators. For a detailed account of these methods reference may be made to that extraordinarily interesting work by Lewis and

¹¹ Sometimes called also the relative activity; for Lewis first defined the absolute activity, as he defined the fugacity, by reference to the attenuated gaseous state, in which the activity was taken as equal to the concentration (*Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907)). More recently, however, it has become the general custom to use the term activity in the sense of relative activity, or relative fugacity, and it is in this sense that we shall use it henceforth.

¹² The term activity coefficient has been used in two senses, sometimes to mean the ion activity divided by the assumed ion molality, and sometimes to express the ion activity divided by the gross molality of the electrolyte. This latter usage, to which we shall find it desirable to adhere in thermodynamic work is more expressly designated by Brönsted (*J. Am. Chem. Soc.*, 42, 761 (1920)) as the *stoichiometrical* activity coefficient.

¹³ For a weak binary electrolyte, when we do not choose to employ the convention that $a_{\pm} = a_+$, we will write $\gamma = a_{\pm}/m$, but we cannot write $\gamma = a_1/m$.

¹⁴ "Ann. Reports on the Progress of Chemistry," 21, 24 (1924).

Randall,¹⁵ in which the authors describe and illustrate many novel applications of thermodynamics to chemical problems. The deviation of actual from ideal behavior may be conveniently expressed by the activity coefficient (a = ratio of activity to concentration), which may be defined as the factor by which the concentrations must be multiplied in order to make the expressions for mass action and free energy applicable to actual as distinguished from ideal solutes. Alternative and independent methods of evaluation are shown to afford consistent values for the activity coefficient."

In other words the activities are the value which one must substitute for the concentrations in order to make the formulas fit. This means that we give up all attempts either to test or to improve our formulas. Lewis implies that his formulas are right because he has deduced them thermodynamically and that consequently he is justified in changing the facts to fit the formula.

The people interested in activities do not care whether the addition of a neutral salt does or does not change the actual hydrogen ion concentration of a solution or not. They are satisfied with their formulas and their formulas fit the facts when activities are substituted for concentrations, in other words when they make the facts fit the formulas. When the history of this period comes to be written, people will probably consider the activity craze as more foolish than the phlogiston theory.

If the addition of a second salt changes the water equilibrium, Debye's very ingenious theory of solubilities becomes a triumph of misapplied skill in calculation.

The general results of this paper are as follows:

1. The displacement of the water equilibrium is apparently the important factor in the peptization of gelatine by potassium iodide solutions and in the effect of neutral salts on pH values.

2. The pH values, as at present determined, stand in no necessary relation to the actual concentrations of hydrogen ion.

3. There is no satisfactory evidence as yet that the addition of sodium chloride to a dilute hydrochloric acid solution causes any increase in the actual hydrogen ion concentration.

4. It is possible that the displacement of the water equilibrium is of importance in causing the variations from the dilution law.

5. The agreement between the potentiometrically determined pH values and those determined by indicators is not an independent confirmation, because both depend on the chemical potential of hydrogen ion and not solely on the concentration of hydrogen ion.

¹⁵ "Thermodynamics and the Free Energy of Chemical Substances" (1928).

6. Since the activities are, by definition, the values which must be substituted for the concentrations in order to make the formulas fit, it is impossible to test the accuracy of the formulas by means of the activity determinations.

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MAKING AND BREAKING EMULSIONS¹

BY WHEELER P. DAVEY

I. Making Emulsions.

The making of emulsions can be most easily described in terms of a definite mechanical picture of emulsion structure. It will therefore be worth our while to give briefly such a picture before discussing the methods of manufacture which have been developed by means of that picture.

For the purposes of this discussion an emulsion may be defined as a colloidal dispersion of one liquid in a second liquid. Usually one of these liquids is water and the other is an oil. The easiest method of making such an emulsion permanent is to have at the interface between the two phases a monomolecular layer of a third substance. In order that such a monomolecular layer may act as an emulsifying agent, not only must the substance be able to spread into a monomolecular layer on either water or oil, but the orientation of the layer formed on water must be opposite to that formed on a hydrocarbon oil. The soaps are characteristic substances of this sort, for one end of the molecule ends in a CH_3 group which can be adsorbed on an oil surface, while the other end is a CO-OM group which can be adsorbed on a water surface. It is upon the structure and dimensions of the molecules of the emulsifying agent that the important physical properties of the emulsion depend.

If the molecules of the emulsifying agent are too short,² as in the case of sodium acetate, each end finds its effect largely nullified by the field from the other end, and the emulsion is unstable. It is only when the molecules are long enough for the substance to be properly called a "soap" that a stable emulsion is formed. In the case of the oil-in-water type of emulsion if the molecules of the emulsifying agent are barely long enough to give a permanent emulsion (for instance sodium laurate) they may be thought of as standing out from the surface of the oil droplet like stiff bristles. We may picture the CH_3 groups at one end of the soap molecule sticking to the CH_3 groups of the oil

¹ Some of the ideas presented in this paper may be found in the published literature, and many in various patent disclosures. Still others are contained in company reports and are given here for the first time. It is the purpose of this paper to give a connected account of the theory of making and breaking emulsions in so far as it seems to the writer to have a sure foundation. No attempt has been made, however, to give the sources of the various items of information.

² For the sake of simplicity, the effect of double bonds is neglected in this discussion.

droplets, and the carboxyl groups tying a film of water to the droplet. Such a picture shows why two such droplets cannot easily coalesce, for when they collide the "contact" is only between two water films, and the droplets of oil never touch each other.

If an emulsifying agent is used whose molecules are somewhat longer (for instance sodium stearate) we may picture the outer ends of the bristles as being so far separated from each other that the adsorbed water film is not quite complete. A collision between two particles of the disperse phase may therefore result in an interlocking of the bristles, thus sticking the droplets together much like two hair brushes pressed against each other. Such an emulsion will slowly gel on continued standing at room temperature, but may be rendered fluid again by vigorous stirring or by heating. The effect of the mechanical stirring or of the heating may be likened to that of shaking the two hair brushes apart. It may be assumed that, if an emulsifying agent with still longer molecules is used, the emulsion will gel more quickly and at higher temperatures.

The bristle picture explains, too, why a gel should have a three dimensional chain structure. It is believed that most ordinary emulsions of the water-in-oil type have a gel-like structure, in which bristles of the emulsifying agent from one oil droplet tend to interlock with bristles from an adjacent oil droplet to give the characteristic stiff structure of the oil phase of such emulsions. The water phase is supposed to be held in the interstices between the chains of oil droplets by the remaining free bristles.

It is at once evident that water-in-oil emulsions can be made in any one of four ways,—(1) an emulsifying agent may be used whose molecules are so long that they cannot disentangle themselves easily at ordinary temperatures, (2) an emulsifying agent can be used whose adsorptive power for water is weak, (3) an emulsifying agent may be used such as a soap containing a polyvalent metal, in which the area covered by the CH_3 groups may be assumed to be considerably greater than that covered by the carboxyl groups tied to the polyvalent metal, (4) the proportion of water to oil may be so low that the oil droplets are compelled to come in contact with each other irrespective of the properties of the emulsifying agent. Further comment on the first and third methods is obviously unnecessary. The second method is considered to be the one employed when the emulsifying agent is an organic acid, such as oleic acid. The fourth method is always found at one stage in the commercial manufacture of oil-in-water emulsions.

Oil-in-water emulsions can be made either with the aid of mechanical agitation or by so adjusting the physical conditions that the emulsification is spontaneous. The first requisite to spontaneous emulsification is that the agent be pretty uniformly dispersed in the oily material which

is to become the disperse phase. The limiting case of this is an ordinary liquid soap, for there every molecule in the disperse phase has the properties of an emulsifying agent. When an alkali-metal soap is to be dispersed in an oil, preparatory to making an oil-in-water emulsion, advantage is taken of the fact that the carboxyl end of the soap molecule attaches itself readily to water. The soap is therefore "dissolved" in water and this "solution" is added to the oil. The mixture is then heated to drive off water until only enough water is left to act as a nucleus at the center of a colloidal droplet of soap. Each droplet is to be thought of as having a radius only slightly larger than the length of soap molecule. Each molecule is pictured as being oriented so that its carboxyl group is attached to a nucleus of water at the center of the droplet. The end containing a CH_3 group is at the circumference of the droplet and is thought of as being attached to the oil. When this condition has been reached, water can no longer be boiled out so easily as before, and the droplets of alkali-metal soap disperse spontaneously in the oil. The amount of water remaining in equilibrium in the nucleus of the droplets of soap is apparently a function of the temperature to which the mass has been heated. In most of the writer's emulsions (mixtures of oils and asphalts dispersed in water) the dispersion of soap in oil was fairly complete at 175°C . The mass was heated, however, to obtain still more complete dispersion to 250°C . with but little further loss of water. The physical structure of the soap-in-oil corresponds to that pictured in ordinary cup grease except that at the temperatures employed the fluidity is such that a sort of creaming seems to occur.

If, now, boiling water is allowed to come in contact with the surface of the oil, a little oil-in-water emulsion is formed spontaneously. The action may be greatly speeded up and made more homogeneous by the following procedure.

(1) The soap-in-oil is heated considerably above the temperature at which the soap first becomes dispersed in the oil. In the writer's experiments the temperature reached was 250°C . This insures the maximum dispersion of soap and therefore the minimum viscosity at the lower temperatures used at a later stage in the process.

(2) Boiling water (so as to have a minimum local cooling effect) is added slowly to the soap-in-oil while it is still quite hot (in the writer's experiments, 200°C .). Stirring by paddles, or by a dough mixer, presents a larger surface for the action of the water, and tends to keep the concentration of water more uniform throughout the whole mass. As the temperature of the soap-in-oil falls, and more and more water is added, the amount of water in equilibrium in the center of the soap droplets becomes greater and greater (phenomenon of "swelling") until finally the threshold of emulsification of oil-in-water is reached for

the temperature employed. The structure is, by this time, to be pictured as a collection of oil droplets each of which is surrounded by bristles of soap which interlock from droplet to droplet to give a network of oil. The water phase is thought of as forming a network in the interstices between the chains of oil droplets.

(3) The addition of more water produces a definite oil-in-water emulsion if only the temperature is high enough to shake the oil droplets apart. By continuing the addition of water a dilution is finally reached which will not gel above the freezing point provided that the soap molecules are not too long.

It has therefore been found possible in terms of a definite picture of emulsion structure to work out a method of making oil emulsify spontaneously in water without the customary vigorous mechanical agitation. The method is free from the necessity of close technical supervision, and is in successful regular factory use under ordinary factory conditions. The customary factory batch is 275 gallons. It may be of interest to note that not a single factory batch made by this method in over seven years has failed to emulsify satisfactorily. It is recognized that the picture on which the method is founded is largely qualitative. Its justification lies in the degree to which it correlates known facts and in the end results which it has produced. It is hoped at a later date to make this picture quantitative by means of a new method for measuring directly the dimensions of colloidal particles, but a discussion of this would be premature at present.

II. Breaking Emulsions.

Breaking an emulsion is defined as the process of causing the disperse phase to coalesce into a mass which is substantially free from the dispersion medium. It is synonymous with curdling. Breaking may be accomplished by (1) mechanical action, (2) concentration, (3) electrodeposition, (4) the "hot-dip," or (5) electrodeposition.

The churning of cream to butter is the outstanding example of breaking an emulsion by mechanical action. The churning is supposed to split open the layer of emulsifying agent (casein) so that the droplets of the oil phase are able to coalesce. A somewhat similar action is reported in the case of dilute water dispersions in mineral oil.

It has already been mentioned that oil-in-water emulsions tend to gel upon concentration. The ultimate limit of this is a breaking of the emulsion. It is especially noticeable during freezing of emulsions which have a soap emulsifying agent. The water phase tends to freeze as pure ice with tiny inclusions of the oil phase. This concentrates the main body of the oil phase so that the droplets are matted together by

the entanglement of the "bristles" of soap, thus giving a curd which is practically water-free. Such a curd can be re-emulsified in the original water by heating to 95° C. The heat motion seems to shake the droplets apart from each other so that each one floats around in the water phase once more, independent of its neighbors. A similar curdling action may be obtained by using a high speed centrifuge.

Each droplet of oil in an oil-in-water emulsion acts as though it carried a charge of negative electricity. This is to be expected if it is once granted that soaps can become ionized in water, for each organic chain of the soap which is attached to an oil droplet would be a negative ion. If D.C. electrodes are inserted in an oil-in-water emulsion it is found that the droplets of oil migrate to the positively charged electrode. If they have a sufficiently high viscosity they will stick to each other and to the electrode, forming a tough spongy coat which holds some of the original emulsion in its pores. From one point of view, this coat may be considered to be a special case of breaking by concentration, the electric field being a method of causing the concentration. This viewpoint is strengthened by the fact that, if such a deposit is placed in boiling water before it has become still more concentrated by the drying of the occluded portion, most of it will wash off to give an oil-in-water emulsion. However, this can hardly be assumed to be a complete picture, for that portion of the coat nearest the electrode does not wash off so easily, showing that the charge on the electrode has altered the structure of that portion of the coat. The electro-deposition of the oil phase from an oil-in-water emulsion seems to follow the ordinary laws of electrolysis in that the quantity of the deposit is proportional to the total quantity of electric charge employed. The process differs from metallic electroplating not only in the reversed signs of the electrodes but also in that it may be carried out successfully at any ordinary voltage. The writer uses voltages from 25 V. to 250 V. Since the coating of "oil" has insulating properties, there is a polarization effect which tends to limit the thickness of coat for any particular voltage.

It is found that if a dense substance such as a sheet of metal or a piece of electrical porcelain is heated to about 250° C. and suddenly plunged into an oil-in-water emulsion, it becomes coated with a layer of the oil-phase. Several theories have been proposed to account for this effect, but none have been completely satisfactory. The most satisfactory theory is that the hot substance raises the emulsion to the boiling point in the immediate neighborhood of that substance and that the oil phase then separates out by concentration in the form of a closely fitting bag.

We have seen that the picture of negatively charged droplets of oil in a soap-stabilized oil-in-water emulsion is consistent with the widely

accepted picture of ionization of soap-molecules. The addition of a small amount of alkali has but little effect, but an excess will (to use the ion-product-constant terminology) repress the ionization of the soap, and should therefore reduce the attraction between the carboxyl group and the water. This makes it possible for the soap films of the droplets to become meshed together upon collision. A salt of an alkali metal has a similar, but very much stronger action. The addition of acid to a soap-stabilized emulsion changes the monomolecular soap films around the droplets from negative ions to neutral organic acid molecules. This in turn reduces the attraction between the emulsifying agent and the water, thus permitting coagulation of the disperse phase. A salt of a polyvalent metal forms a so-called "metal soap," thus causing coagulation just as before. A somewhat similar picture may be made of casein-stabilized emulsions and emulsions with other amphoteric emulsifying agents when brought near their isoelectric point. In such cases, the changes to be made in the detailed pictures given above are obvious.

From the foregoing, it is evident that the same plausible picture of emulsion structure given at the beginning of this paper gives a rational explanation not only of the methods of making emulsions, but also of the methods of breaking them.

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EMULSIFICATION: I. A STUDY OF OIL SOLUBLE EMULSIFYING AGENTS

BY BRIAN MEAD AND JOHN T. MCCOY

Introduction:

It is generally accepted that interfacial tension lowering and emulsification power are very closely related. Some go so far as to say that interfacial tension lowering is the controlling factor in emulsification.¹ This much is certain, that those substances which lower the surface tension of water do also act as emulsifying agents for oil in water. The mechanism by which the stabilization occurs has been variously explained. Thus Bancroft² has postulated a film of molecules of emulsifying agents around the globules of dispersed phase. This film may be considered as being held in position by the forces of adsorption. By lowering the surface tension on the water side of the interface, the film is so curved that it eventually actually encloses a drop of oil and prevents its coalescence with another similarly enclosed drop.

The oriented wedge Theory of Langmuir-Harkins³ is of a different type altogether. It has as its main postulate the polar nature of the substance which acts as emulsifying agent. This results in one part of the molecule being strongly attracted by, and imbedded in, the water, while another is equally strongly held in the oil phase. This results in an extremely strong bond between the two phases.

It has long been recognized that oil-water emulsions may be of two types: First, those in which the oil is dispersed in a continuous medium of water and the second with these phase relations reversed. In either case it is necessary, in order that a stable emulsion may result, that there be a suitable emulsifying agent dissolved or dispersed in the continuous medium. Of such agents which stabilize the oil-in-water type of emulsion the most prominent examples are the water-soluble soaps. It is possible also to use a number of insoluble finely divided solids⁴ which are relatively more readily wet by water than they are by oil, to achieve the same end. Such powdered materials will concentrate at the interface between the oil and the water, and

¹ Hillyer, *J. Am. Chem. Soc.*, **25**, 513 (1903); White and Marden, *J. Phys. Chem.*, **24**, 617 (1920).

² "Applied Colloid Chemistry," 261 (1921).

³ Harkins, Bogue's "Colloidal Behavior," 142-210 (1924).

⁴ Briggs, *Ind. Eng. Chem.*, **13**, 1008 (1921); Pickering, *J. Chem. Soc.*, **91**, 2002 (1902); Schlaepfer, *J. Chem. Soc.*, **113**, 522 (1918).

so will stabilize the oil drops in the water. These powders, however, do not have any effect on surface tension.

On the other hand, soaps of the polyvalent metals will dissolve more or less readily in the oil phase and not at all in water. They stabilize the opposite type of emulsion, in which the water is dispersed in oil.

A great deal of work has been done in the past on the determination of the emulsifying tendencies and characteristics of the water soluble emulsifiers, and we are now in a position to draw some conclusions as to the manner in which they act. Whilst the emulsions resulting from the use of such materials are of considerable importance in pharmacy, it is with water-in-oil emulsions, their stability and resolution, that oil technologists are primarily concerned. It is this type of emulsion which confronts them in the oil fields and to which they have to devote so large an amount of thought and energy. Many of the chemical, mechanical, and electrical methods which are actually utilized for the breaking of such emulsions are the result of empirical methods which have little or no scientific basis. It is known that certain methods have been successful in dealing with emulsions from specific localities whilst they are quite useless for emulsions coming from a different source.

Considering, for example, the well known Tret-o-lite⁵ method of breaking crude emulsions, Tret-o-lite, a patented compound, contains

Sodium oleate	83.0%
Sodium resinate	5.5
Sodium silicate	5.0
Phenol	4.0
Paraffin	1.5
Water	1.0

Sodium oleate is partly soluble in oils, and yet it is not this solubility alone which is the cause of the breaking of the emulsion which results when this reagent is agitated with a crude-oil emulsion. Sodium oleate alone will not cause such a separation. What happens in such cases is that the sodium oleate will emulsify drops of oil in the water phase, these oil drops themselves having water emulsified in them. If such a complex emulsion be now treated with any of the salting-out agents (any acid or a salt of a monovalent metal) the oil-in-water emulsion is broken but there still remains a great deal of water emulsified in the oil which so results. We can, however, by the addition of phenol to the sodium oleate in the proportions required by the tret-o-lite formula, cause an actual breaking of the water-in-oil emulsion, even though in this case, too, we may get an intermediate formation of an oil-in-water emulsion which it will be necessary to break by the addition of a salting out agent. By the use of such a mixture it is possible

⁵ Mathews and Crosby, *J. Ind. Eng. Chem.*, **13**, 1015-16 (1921).

to obtain results which are entirely comparable with those obtained by using the complete ingredients called for by the tret-o-lite formula, so that the efficiency of the formula would seem to be dependent largely, if not entirely, upon the presence of the sodium oleate and the phenol. Moreover, it is a comparatively simple matter to get considerably better resolution in many cases by the use of ⁶ other phenolic substances than phenol itself. Thus, unpublished work in this Laboratory has shown conclusively that by the use of poly phenols which are successively more and more acidic in character, it is possible to get more and more complete resolution of the emulsion.

In view of these considerations it is not unjustifiable to draw the conclusion that by the interaction of sodium oleate and e.g. phenol, we form sodium phenolate and oleic acid. This latter is readily soluble in such oils as form the basis of the emulsions under consideration. On the basis of any of the various theories of emulsification, if we are to be able to break an emulsion, we must be able to attack the interface between oil and water by the breaking agent we are using. It may well be that the function of the oleic acid, formed as has been postulated, is just to attack the film of whatever emulsifying agent it is which is surrounding the particles of dispersed water and stabilizing them.

Experimental Procedure:

A modified form of stalagmometer was used for the determination of the interfacial tension which exists between a sample of oil and pure water. This consists essentially of a small pipette, the lower extremity of which is sealed into a capillary tube, the exposed end of which is very carefully ground off to a plane surface at right angles to the axis of the pipette. This grinding is accomplished by imbedding the glass tube in Rose metal, grinding it on successively finer emery wheels and subsequently removing the metal by dipping in hot water. It has been shown by previous workers on interfacial tensions that the time of formation of drops in such an apparatus very largely controls the size of the resultant drop. In view of this, a drop formation time of one minute was maintained throughout the experimental work. The Lohmstein Harkins correction for the size of the drop was applied in each case.⁷ The rate of drop formation was controlled by means of a capillary tube through which air entered to the top of the liquid in the pipette. This gave extremely sensitive and accurate control of the time of drop formation. A number of such capillary tubes was prepared ahead of time and a suitable one was taken for each set of experiments. Extreme precautions were taken to insure that the ground

⁶ Lyon, Thesis, Chem. Eng., 1923, Mass Inst. Technology.

⁷ Harkins, *J. Am. Chem. Soc.*, 41, 499 (1919).

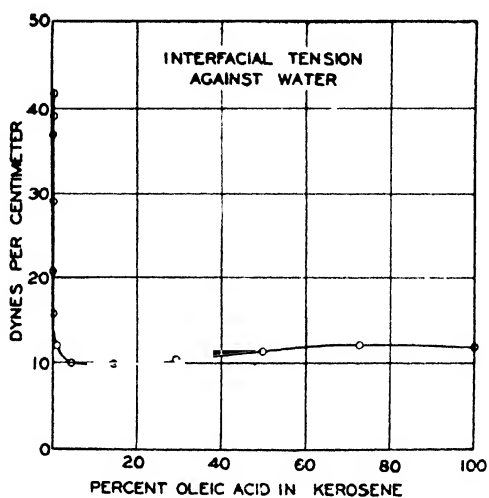


FIG. 1.

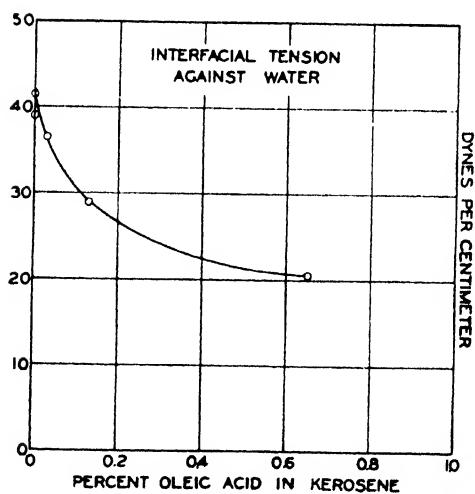


FIG. 2.

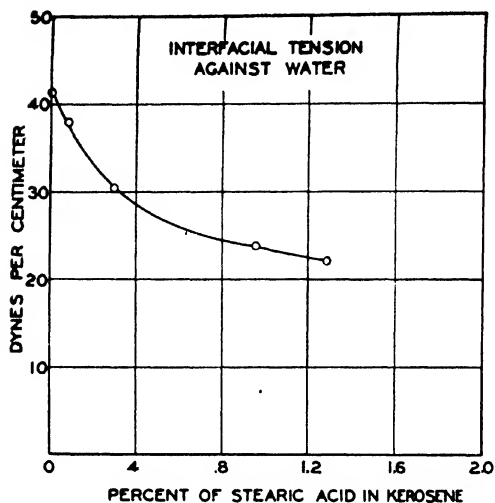


FIG. 3.

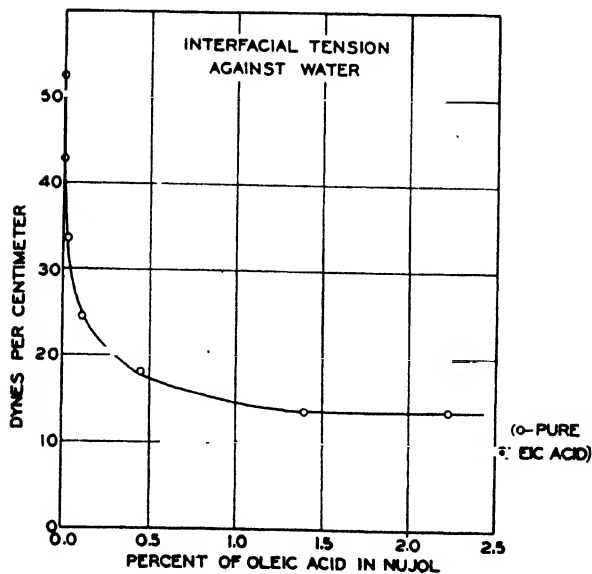


FIG. 4.

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glass tip of the capillary was completely wetted by water before each determination of the drop number.

In order to appreciate and to understand the action of the oleic acid, the first and most obvious step was to dissolve some of it in oil and to determine the effect which it had on the interfacial tension between oil and water.

Similar reasoning being equally applicable to the case of sodium stearate, since experiments showed that it could be substituted for

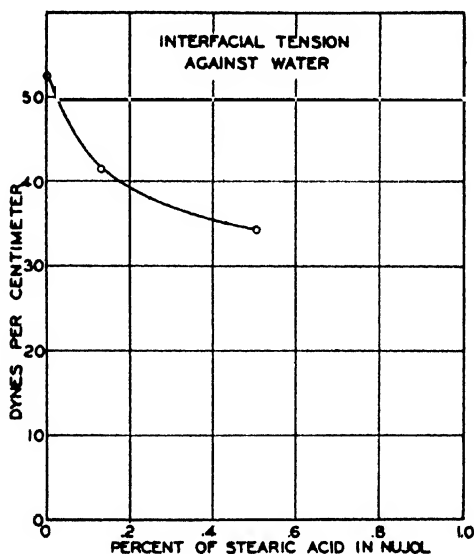


Fig. 5.

sodium oleate with satisfactory results, a further set of determinations was made as to the influence of stearic acid as the oil-water interfacial tension. The results are shown graphically in Figures 1-5. The curves show very clearly that the effect is an adsorption phenomenon, the characteristic shape for such curves being obtained in each case. After the addition of a comparatively small amount of either acid to the oil in question, the interfacial tension is lowered approximately to the same extent as by an addition of 90 per cent of the acid. Such an effect can only be caused by an adsorption phenomenon. Two different oils were used for this purpose—kerosene and nujol, and in both cases, this type of result is obtained. It is rather interesting to note that

oleic acid lowers the interfacial tension very much more than stearic acid, a result which might be expected in view of the fact that stearic acid is the saturated form of oleic acid. At the temperature of our experiments, sodium oleate is a much more efficient emulsifier than sodium stearate. It is interesting also to note that if we plot (as is done in Figure 6); the percentage lowering of the interfacial tension against the percent of acid added to oil, we obtain identical curves for the use of one acid on either oil, nujol or kerosene. The same differ-

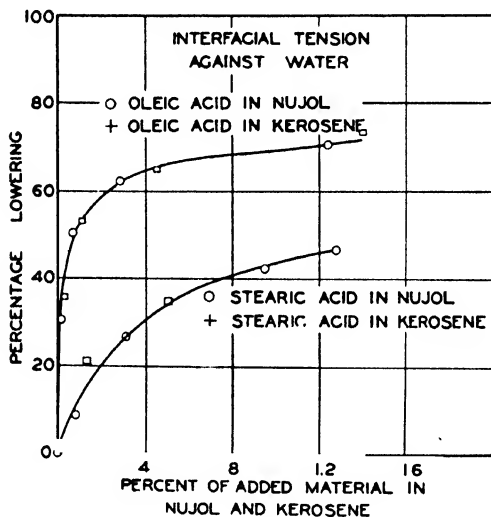


FIG. 6.

ence between the effect of oleic and of stearic acid is, of course, maintained in this case.

In view of this difference between the effects on interfacial tension exhibited by the saturated and unsaturated forms of the same acid it is of interest to speculate on the influence of unsaturated compounds in general on the emulsification power of oils and on the interfacial tension between such oils and water. Crude oils are known to contain unsaturated compounds, and are known to emulsify, in some cases, considerable quantities of water, without the addition of any further stabilizing agent. Of course, in some cases a contributing, or even the controlling, cause of emulsification is the presence of finely divided materials which, being preferentially wet by oil, act as emulsifying agents for the water with which the oil is in contact underground

before it comes to the surface. But even if such finely divided materials be removed from the oil there is still a great tendency for emulsification to take place. As the oil is progressively freed from unsaturated components in the refining process, it exhibits less and less tendency to emulsify water.

Parsons and Wilson⁸ took amylene as a type of the unsaturated compound which might well exist in a crude oil, and they showed that amylene stabilized oil-in-water emulsions, the degree of stabilization being roughly proportional to the concentration of added amylene.

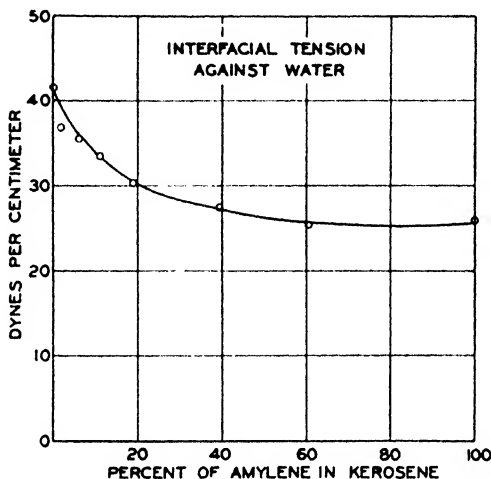


FIG. 7.

They tested its stabilizing influence by making emulsions containing various amounts of it, and determining the equivalent concentration of sodium chloride necessary to break the emulsions. It is to be noted that in their experiments they first made an emulsion of nujol in water by the use of sodium oleate and then added to this emulsion amylene in various concentrations. They specifically state that the amylene, when shaken with water gives a rather unstable emulsion (presumably amylene in water). Since the amylene is not appreciably water soluble there is, by virtue of the sodium oleate present in the system, little or no chance for the amylene to dissolve in the emulsified oil drops but it rather remains emulsified in the water. Hence it is not present in the system under conditions comparable with those

⁸ *J. Ind. Eng. Chem.*, 13, 1116 (1921).

obtaining in industrial practice, in which case it is actually dissolved in the oil. The increased amounts of salt which were necessary to break emulsions containing amylene may very well have been utilized in breaking the amylene emulsions and not the nujol emulsion proper.

In the experiments reported in this paper the amylene was actually dissolved in the oil phase-kerosene in this case—and the resultant effect on the oil-water interfacial tension determined. The results are given in Figure 7 and show once again the same type of adsorption curve as was obtained for oleic and stearic acids. The relative effect of amylene is, however, considerably smaller than that of either of the two acids. There is, moreover, not the same sudden drop in interfacial tension consequent upon the addition of very small amounts of amylene, followed by a long period when the addition of further amylene has no effect on the tension. In this case the effect is progressively greater as we approach a solution containing 100 per cent amylene and no kerosene.

It had been intended to determine the lowering obtained by the use of a number of oil soluble (heavy metal) soaps of the interfacial tension between oils and water, but it was found to be impracticable to do so. The main objection to the procedure lay in the fact that most of the heavy metal soaps were not readily soluble in oil. To get them into solution required heat and this changed the interfacial tension of the oil itself, against water, in a very erratic manner. Of those which required little heating to get solution the results are given for zirconium stearate and aluminum stearate. The zirconium stearate was prepared by metathesis from zirconium nitrate and sodium oleate. The soap was precipitated in an extremely finely divided condition, and this on vacuum drying caked. It appeared to melt at about 60° C. When heated in a platinum crucible and ignited, it continued to burn for some time. 0.8390 gram of the substance yielded 0.1551 gram of ignited residue. If the formula $\text{Zr}(\text{OH})_2\text{St}_2$ be assumed, this would require an ash (ZrO_2) of 0.148 gram, which checks reasonably with that found by experiment.

As will be seen from Figure 8 the amount of lowering produced by this substance was not great. The curve followed the same general lines as those for oleic and stearic acids. Apparently in this case maximum lowering is produced by as low a concentration as 0.9 per cent. With oleic acid this figure was 2 per cent and for stearic acid it was not determined but was probably in the same range. The maximum lowering produced by zirconium stearate was from 51.7 to 44.5 dynes/cm, or 14 per cent.

Aluminum stearate was prepared by metathesis and precipitated as a white powder which was readily dried. It melted at about 120° C. and solvated in nujol at about 90° to form, on cooling, a clear solution.

It was not at all readily soluble in oil and only a few determinations were made with it. It did, however, lower the nujol-water interfacial tension from 35.5 to 32.2 dynes/cm at a concentration of 0.217 per cent, a lowering of 9.3 per cent.

Magnesium oleate. Also made by metathesis, was a horny material (probably containing free oleic acid by decomposition of the oleate) which appeared to melt at 80° C. In the first experiments it solvated

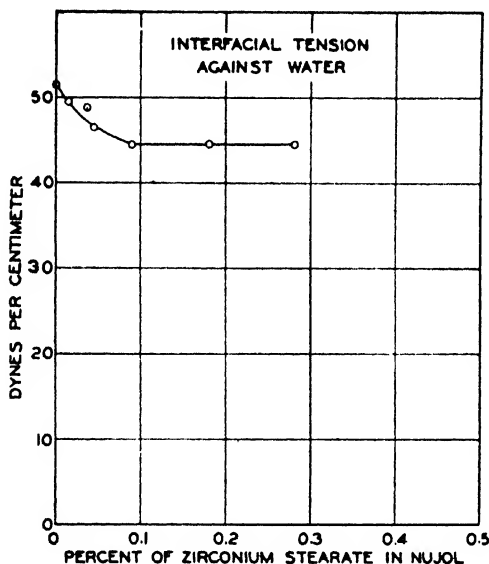


FIG. 8.

in oil at 100° C. to give a clear solution, but later attempts to dissolve it were unsuccessful, it forming sticky yellow aggregates.

Magnesium stearate. Made by metathesis, was a white fluffy powder, melting at about 145° C. It solvates in nujol at about 120° C. to give a clear solution on cooling.

Aluminum oleate. Was made by metathesis. As made, it was a rubber-like curd which agglomerated to a sticky plastic mass (probably due to the presence of free oleic acid formed by hydrolysis of the oleate). It becomes fluid at 120° C. It solvates in nujol at a temperature not less than 200° C., to yield a viscous homogeneous mass. The cold solution exhibits unusual properties. When stirred it shows the normal elasticity of a gel. On the other hand it does flow ex-

tremely slowly, acting as a liquid of high viscosity. We have here an exaggerated example of a colloidal solution which is both fluid and elastic.

Zinc stearate. A white powder, melting at about 140°C . It solvates in oil at about 100°C . to give a clear solution. On cooling, however, turbidity develops, precipitation occurring.

Sodium oleate. In the course of some work on the emulsification power of sodium oleate⁹ it was found that this soap, in aqueous solu-

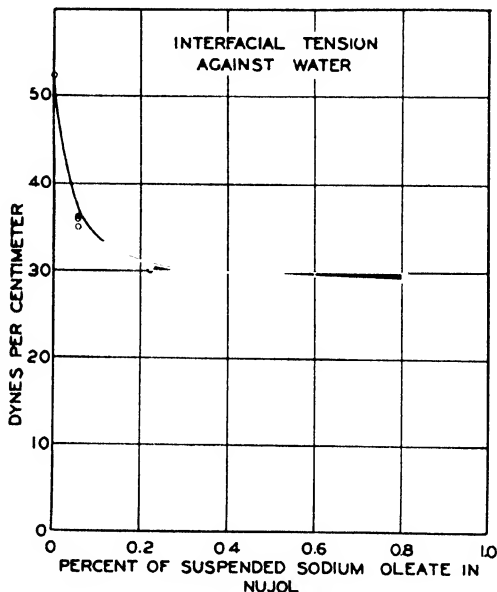


FIG. 9.

tion, deteriorated ("aged") very markedly. Eventually it was possible for a sodium oleate solution actually to give an emulsion of the water-in-oil type, a complete reversal of its normal emulsification tendency. It seems probable that this reversal was due to solution in the oil of some of the hydrolysis or degradation products of the sodium oleate. In other experiments it was found that if an emulsion were made with sodium oleate as the emulsifying agent, this emulsion being then broken by the addition of sodium chloride, and the whole system allowed to stand for a time, some of the soap dissolved in the oil phase. If now

⁹ Reported at Baltimore Meeting Am. Chem. Soc., 1925.

the whole system were re-stirred vigorously, an emulsion of the opposite type would result (water in oil). Very evidently in this case also the sodium oleate was acting in a sense opposite to the normal. It is to be clearly understood that in neither case was the emulsion as stable as the ordinary type of oil-in-water. It could, moreover, be reversed by addition of water and agitation. The results were, however, reproducible and unmistakable.

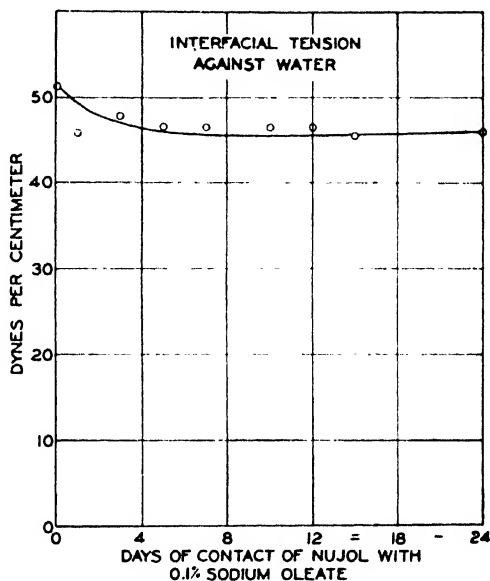


FIG. 10

In view of these experiments a number of determinations were made on the effect of sodium oleate, when dissolved or suspended in nujol, on the nujol-water interfacial tension. When the soap was just stirred into the oil, and allowed to settle before determination of the interfacial tension against water, the results were very erratic and incapable of analysis.

However, when the interfacial tension was determined while the oleate was still in suspension in nujol, very good checks were obtainable, and the results obtained are given in Figure 9. These results are not at all comparable with the lowering which is obtained in the surface tension of solutions of sodium oleate in water. In such a case the tension would be reduced by the oleate to a value of about 25 dynes/cm

for a 0.05 per cent solution. Mere contact with a sodium oleate solution does not change the interfacial tension of the oil against water to the same extent. Figure 10 shows the effect given by contact for a

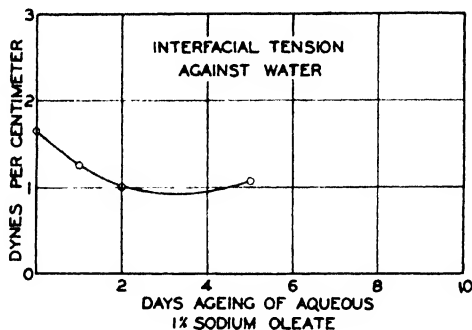


FIG. 11.

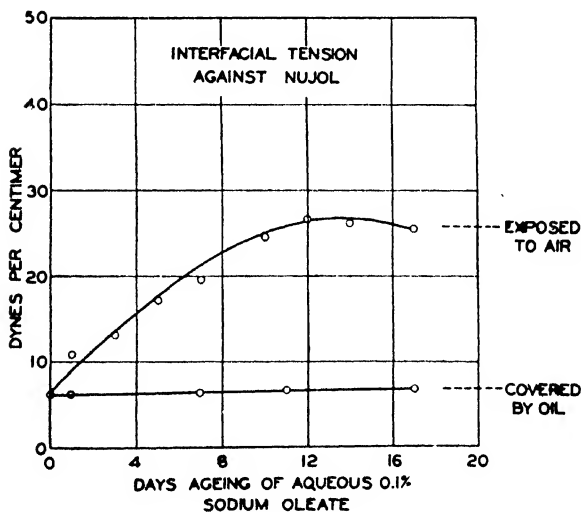


FIG. 12.

period of time up to 24 days of nujol with 0.1 per cent sodium oleate solution. It will be seen that in two days the tension changes from 51.5 to about 45 dynes/cm, thereafter remaining sensibly constant for 22 days' further exposure.

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Concerning the aging of the sodium oleate solutions, as mentioned above, a 1 per cent solution if allowed to stand in contact with air will actually age so badly as to give eventually a water in oil emulsion. The results obtained with such a solution are given in Figure 11. It will be seen that in such a case, the tension drops at first, to pass through a minimum, and ultimately rise again. The results are not very accurate, since to measure such extremely low interfacial tensions was outside of the province of the apparatus used.

It is interesting to see the effect on the interfacial tension of a 0.1 per cent solution of sodium oleate against nujol, of covering it with oil. Figure 12 shows clearly that when the soap solution is covered with oil its tension remains constant, whereas when it is freely exposed to air the tension rises steadily for 13 days, thereafter decreasing again. This experiment clearly indicates that the mechanism of aging is not due to hydrolysis of the sodium oleate but to the interaction with it of some atmospheric constituent. It will be of great interest to follow up this phenomenon more thoroughly.

Summary.

1. The effect on the oil-water interfacial tension of solution of oleic and stearic acids and of amylene in the oil has been determined.
2. A similar determination has been made of the effect of zirconium and aluminum stearates. Other heavy metal soaps were either insoluble in the oil or so increased the viscosity as to render the determinations impracticable.
3. The effect on the oil-water interfacial tension of sodium oleate, suspended in oil, has been determined.
4. The surface tension of a sodium oleate solution has been measured, and the changes with time noted.

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THE MECHANICS OF ADSORPTION AND OF THE SWELLING OF GELS

BY CHARLES TERZAGHI

In an attempt to correlate the results of previous investigations concerning the elastic expansion of coarse grained soils with the results of the investigations concerning the swelling of elastic gels, I was startled by the close relationship which exists between these two groups of apparently very different phenomena. The following paper represents an attempt to explain the causes of this relationship and to correlate them with the current conceptions concerning the nature of the adsorption phenomenon.

Relation Between Swelling Pressure and Vapor Pressure.

By thermodynamic methods J. R. Katz¹ has derived, for the swelling pressure P the formula

$$P = - \frac{RT}{MV_0} \ln h \quad (1)$$

where M = the molecular weight of the liquid contained in a gel,

V_0 = the specific volume of this liquid,

T = the absolute Temperature,

R = the Gas constant,

P = the pressure exerted by the gel at a certain concentration per unit of surface of a rigid obstacle when swelling,
and

h = the relative vapor pressure of the gel at the same concentration.

The same equation has been obtained by H. Freundlich² from a thermodynamic analysis of the following isothermal process: A quantity dw of a liquid is transferred from a gel I, exerting a swelling pressure P_1 into a swelling gel II of the same type, but exerting a swelling pressure P_2 . If dV is the volume occupied by the quantity dw of liquid, the work performed during the transfer is $(P_1 - P_2)dV$

¹ *Kolloidchem. Beihefte*, 19, 1-182 (1918).

² "Kapillarchemie," 930 (1922).

Then the quantity dw is distilled back from the gel II to the gel I which requires an amount of work

$$- \frac{RT}{M} \ln \frac{h_1}{h_2} dw$$

wherein h_1 and h_2 indicate the vapor pressures of the gels I and II respectively. Since the process is supposed to be isothermal, both amounts of work must be equal. The equation thus obtained also leads to the formula (1).

On the other hand, based on the results of numerous Ödometer tests, H. Freundlich and E. Posnjak² have derived an empirical relation which exists between the swelling pressure, measured by the Ödometer method and the concentration of the gel.

Let Q be the swelling pressure in grams per cm.²,

c the concentration (grams of dry matter per 1000 cc. of dry matter and liquid),

k a coefficient whose value varies, according to the nature of the gel between the extreme limits 2.48 and 4.13, and

Q_0 a constant, characteristic for the gel.

$$Q = Q_0 c^k. \quad (2)$$

According to both Freundlich and Katz, the values P' and Q expressed by the formulæ 1 and 2 should be identical. Very few empirical data are available thus far for checking whether this assumption is justified or not. However, the few data which are at our disposal disclose a striking discrepancy between the figures computed by means of the formulas (1) and (2) respectively. In Figure 1 the abscissæ represent the swelling pressures and the ordinates the void-ratio (relation between the volume occupied by the liquid and the volume occupied by the solid phase) of a gelatine gel. The abscissæ of the plain curve C_2 represent the swelling pressures computed by Freundlich from the results of Ödometer tests by means of the formula

$$Q = 0.00002704 \cdot c^{2.9713}$$

and the abscissæ of the dotted curve C_1 were computed from the results of vapor pressure determination for gelatine by means of the formula

$$P = - \frac{RT}{MV_0} \ln h = - \frac{0.0821 \times 293}{18 \times 1.00} \times 1000 \times \ln h = -1442 \ln h.$$

The Ödometer tests and the vapor pressure observations have been performed with two different gelatine preparations which certainly

² *Kolloidchem. Beihefte*, 3, 417 (1912).

may account for part of the difference between the results. But the figure shows not only a tremendous difference between the numerical values, but also a fundamental difference in the character of the curves.

One of the causes of the disagreement seems to reside in Freund-

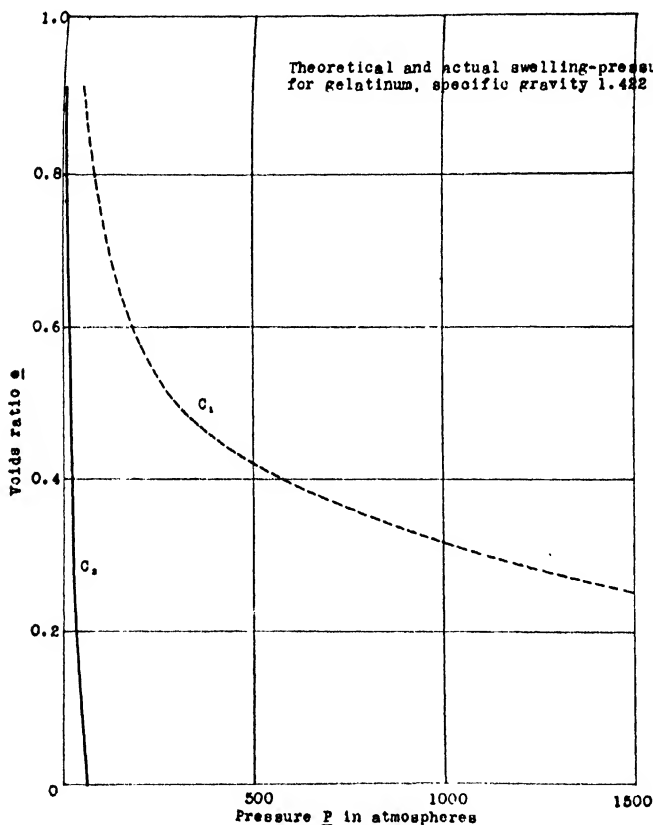


FIG. 1.

lich disregarding the fact that part of the volume of the gel is occupied by solid matter. His formula should be provided with a correction factor, to allow for this fact. This correction factor can easily be obtained by applying the laws of hydrostatics to the problem in question. Provided the physical characters of the capillary water

be identical with those of ordinary water, the low value of the vapor-pressure merely indicates that the water is in a state of tension. This becomes particularly obvious if deriving the vapor-pressure formula in the following manner:

Consider two bodies of water of which the body I is under no stress ($P = 0$), while the body II is in a state of tension, the intensity of the tension being equal to P per unit of surface. The vapor pressures should be h_1 and h_2 respectively. If we transfer a quantity dw of water with a volume dV from body II to the body I, the work performed is equal to $P \cdot dV$. On distilling it back again, one has to perform an amount of work:

$$- \frac{RT}{M} \ln \frac{h_2}{h_1} dw.$$

Hence

$$P dV = \frac{RT}{M} \ln \frac{h_2}{h_1} dw \quad \text{or}$$

$$P = \frac{RT}{M} \ln \frac{h_2 dw}{h_1 dV} = \frac{RT}{M V_0} \ln \frac{h_2}{h_1}. \quad (3)$$

If applying this formula to the vapor pressure on the surface of a small drop with a radius r , we must replace the pressure P by the pressure exerted by the surface tension t . This pressure is equal to

$$P = \frac{t \cdot 2\pi r}{r^2 \pi} = \frac{2t}{r}$$

hence

$$\frac{2t}{r} V_0 = \frac{RT}{M} \ln \frac{h_2}{h_1}$$

which represents the well-known vapor pressure formula for a small drop.

The tension which exists in the capillary water of the gel must obviously be compensated by an equal and opposite pressure acting in the solid phase, because the system is supposed to be in a state of equilibrium, which involves that, for every ideal cross-section of the system, the sum of the internal forces must be equal to zero. If we reduce the tension P in the water to zero, by freely admitting the water through a semi-permeable membrane, while at the same time preventing the expansion of the gel, the gel exerts against the constraining obstacle a swelling pressure. This swelling pressure is equal to the pressure under which the gel stood, before the water was admitted, and this pressure in turn is equal to the total tension which previously existed in the water. These statements strictly represent

the mechanical meaning of Freundlich's computation. However, in drawing his final conclusions, Freundlich assumed that the tension in the water acted over the *whole* cross-section of the gel, while in fact it acted only over part of it. In order to consider this fact, we have to proceed in a manner similar to that which we would use to compute the swelling pressure of a compressible, porous body of the type represented in Figure 2. Since the voids of this body are supposed to

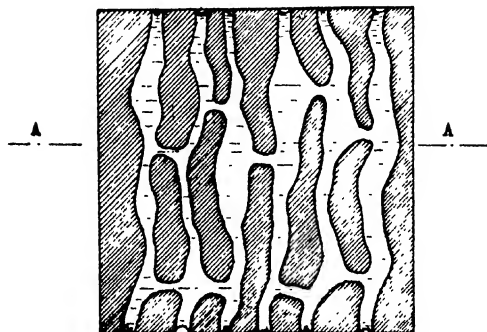


FIG. 2.

communicate with each other, the menisci will have, in every one of the openings, the same radius of curvature, corresponding to a vapor pressure h and to a tension P in the water.

Let F be the total area of a cross-section AA of the body,

F_1 the total area of the cross-section of the voids of the body in the same plane AA ,

$F_2 = F - F_1$ the area of the cross-section of the solid part of the body in the same plane.

The total tension acting in the water along the plane AA is equal to $P \times F_1$.

If we reduce the tension in the water to zero, at the same time preventing a corresponding elastic expansion of the porous body, this body will exert a total swelling pressure equal to $P \times F_1$, or of

$$P_1 = P \times \frac{F_1}{F} \text{ per unit of area.} \quad (4)$$

However an investigation of the correction factor for clays seems to have shown, that the correction factor is very small, even for high con-

centrations. Hence the correction can account only for a small part of the difference. As a matter of fact, there is still another and more important point in Formula 1, which seems to be open to objection. In deriving this formula, it was assumed that the specific volume of the liquid in the gel was identical with the specific volume of ordinary water, and the investigations of W. D. Harkins⁴ leave no more doubt that it is considerably smaller. This fact invalidates the assumption on which the formula was based. In addition, it leads one to suspect that, for gels with very narrow openings, the lowering of the vapor pressure not merely indicates the presence of a mechanical stress in the liquid, but that it *also expresses an alteration of the molecular state of the water*. Further discussion of the vapor pressure formula will lead to similar conclusions.

Vapor Pressure and Size of Micropores of Gels.

Before proceeding to a discussion of the vapor pressure formula, some remarks should be made concerning the probable width of the micropores of the gels.

In 1914 J. S. Anderson⁵ published a formula which expresses the relation between the vapor pressure and the radius of micropores. Since then the formula has been assimilated into many textbooks on capillary chemistry. It gives remarkably small values for the diameter d of the voids of gels (e.g., for Silica gels at the point of "change of color"; the voids filled with water, $d = 5.492 \mu\mu$; with alcohol, $d = 5.174 \mu\mu$, with Benzol, $d = 5.980 \mu\mu$. For the lower point of transition, $d = 2.752, 2.424$ and $2.702 \mu\mu$ respectively. However, Anderson's formula is based on the assumption that the lowering of the vapor pressure merely expresses the presence of a tension in the liquid and that the physical properties of the liquid contained in the voids, particularly the surface-tension, are normal.

In contradiction of this, as a result of an investigation of the physical properties of clays I was led to the conclusion that both the surface tension and the viscosity of the water contained in the voids of very fine-grained powders are greater than in normal water, the discrepancy rapidly increasing with decreasing size of the voids. For the viscosity of water in narrow openings I derived the empirical formula

$$\eta'_0 = \eta_0 \left(1 + \frac{6.02 \cdot 10^{-42}}{s^8} \right) \text{ to } \eta_0 \left(1 + \frac{2.42 \times 10^{-43}}{s^8} \right) \quad (5)$$

⁴ *J. Am. Chem. Soc.*, **43**, 1787 (1921)

⁵ *Z. physik. Chem.*, **88**, 1914 (1914)

⁶ *Z. angew. Mathem. und Mech.*, **4**, 107-113 (1924).

wherein ν_0 = the viscosity of normal water at room temperature in absolute units,

ν_0' = the viscosity of the water in a slit with a width $2s$ (in cm.) at the same temperature.

Since this formula was published I learned of the important observations made by W. D. Harkins⁷ concerning the density of liquids contained in the micropores of gels. According to the statements of Harkins the density of water contained in the voids of charcoal is of the order $1:0.75 = 1.33$, corresponding to the density of water under a pressure of more than 20,000 atmospheres. The density in turn is intimately connected with surface tension. With the present state of our knowledge it is not possible accurately to compute the increase in surface tension due to this increase in density. This is particularly true because we have as yet no clear conception of the molecular state of the adsorbed liquid. However, to get some idea of the order of magnitude of this influence, we may first apply a formula, derived by R. O. Herzog⁸ from Van der Waals' equation, but valid for non-associated liquids only. Let

ν be the specific volume of the liquid,

T_k the critical temperature (absolute),

T any Temperature,

a and b the constants in Van der Waals' equation,

A and B two other empirical constants, and

t the surface tension of the liquid.

According to Avenarius, the equation

$$\nu = a - b \ln (T_k - T)$$

should be valid within very wide limits. For the surface tension Van der Waals has derived the equation

$$t = A \left(1 - \frac{T}{T_k} \right) B$$

Combining these two terms, we obtain

$$\ln t + \frac{B}{b} \nu = \ln A + \frac{aB}{b} - B \ln T_k.$$

By substituting $\frac{B}{b} \nu = r$ and $\ln A + \frac{aB}{b} - B \lg T_k = s$, both quantities r and s being independent of the temperature, we obtain

$$\ln t + r\nu = s \quad (6)$$

⁷J. Am. Chem. Soc., 43, 1787-1802 (1921).

⁸Z. Elektrochem., 14, 830 (1908).

or for water, computed from the densities at 4° and 80° respectively,

$$\ln t + 8.29v = 12.62.$$

Introducing into the equation the value for v of adsorbed water computed by Harkins, we obtain

$$\ln t + 8.29 \times 0.75 = 12.62$$

or

$$t = 600 \text{ Dynes,}$$

a value which is *eight times greater* than the value of the surface tension at room temperature. This calculation obviously is based on the assumption that the decrease in the specific volume was caused by lowering the temperature at constant pressure. As a matter of fact, for reasons which will be presented later, we are inclined to believe that the molecular state of the adsorbed layer resembles much more a state produced by undercooling than a state produced by high pressure.

If, on the other hand, we assume that the increase in density is due to raising the pressure at constant temperature we can, as a first approximation, assume that the surface tension is proportional to the total internal pressure, i.e., to the intrinsic pressure p_0 at normal temperature plus the external pressure p . According to Van der Waals' equation, the value p_0 should be of the order 11000 atmospheres, while the value p is according to Harkins equal to or bigger than 20000 atmospheres. Hence

$$t = t_0 \frac{p + p_0}{p_0} = t_0 \times \frac{31000}{11000} = 2.82 t_0. \quad (7)$$

So that in this case, the surface tension should be about three times greater than the normal value of the surface tension.

As a result of these computations we can hardly avoid the conclusion that the surface tension of the water contained in the micropores of the gel is considerably greater than the normal value of this tension. In addition, we shall find later on that the lowering of the vapor-pressure seems to be due not only to the tension in the liquid but also to a change in the molecular state of the liquid. As a consequence, it is very probable that Anderson's formula furnishes for the diameter of the voids of gels values which are considerably too small.

Harkins Pressure Hypothesis.

Reference has been made to the investigations of W. D. Harkins. These investigations have furnished conclusive proof that the density of liquids contained in the voids of gels is considerably greater than

the density of the same liquids if contained in macropores. The increase in density due to adsorption was found to be remarkably proportional to the compressibility of these liquids. Based on these facts, Mr. Harkins concluded that the adsorbed liquid exists under pressures of more than 20000 atmospheres.

The discovery of Mr. Harkins undoubtedly represents one of the most important steps towards a fuller understanding of the nature of the process of adsorption. However, the conclusions derived from the results of the observations seem to be somewhat in contradiction with two well established facts:

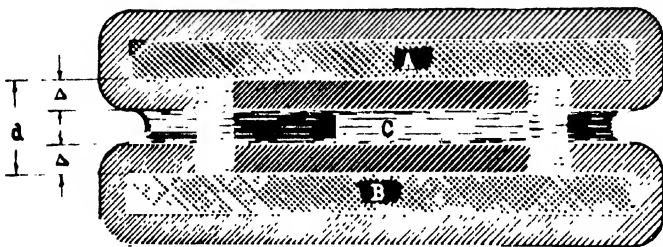


Fig. 3.

The first one concerns the range of molecular attraction. High pressure in the adsorbed liquid could not possibly be produced except by intense molecular attraction by the molecules of the solid, an attraction acting over a distance many times greater than the diameter of the molecule. Thus far neither the investigations of molecular interaction between the molecules of gases nor those concerning their interaction in solids furnish any evidence for the existence of such forces. On the contrary, all the results tend to demonstrate that the molecular attraction is limited to a sphere whose radius hardly exceeds the diameter of the molecule. Hence the diameter of the sphere of intense attraction is very small if compared with the values furnished by Anderson's formula for the diameter of the voids and it was pointed out that even these values may be considerably smaller than the true ones.

The second fact which seems to be incompatible with Harkins' hypothesis concerns the state of stress existing in the liquid. The lowering of the vapor pressure indicates according to formula (3) a *tension* in the liquid. In a gel with narrow voids, where the increase in density extends across the whole cross-section of the voids, the intense corresponding pressure should produce a marked increase in

the vapor pressure. To illustrate the physical consequences of Harkins' hypothesis, I propose the following analogy:

In Figure 3 the two plates A and B represent the solid phase of the gel, the springs provide the elastic resistance of the gel against the reduction of the volume of voids by pressure (external or internal pressure). The liquid phase is enclosed between the two plates and, within a zone of the thickness λ , it is supposed to be intensely attracted by the material of the plates. Hence, on account of this attraction, each one of the plates will be surrounded by a layer of thoroughly compressed liquid, and the attraction between the plates will be due to the surface tension of the non-compressed liquid between the compressed layers. The cross section of this body of non-compressed liquid is called C and is indicated in the figure by a blank space. If the liquid evaporates, the area C becomes smaller and smaller until it finally disappears. The disappearance of the area C is accompanied by that of the menisci, hence, on further evaporation, the attraction between the plates A and B could not possibly be due to any force other than the attraction of plates A and B across the space occupied by the compressed liquid. At the same time the vapor-pressure should increase rapidly and, according to equation 3, it should finally reach fantastic values. It does not seem that such a conception of the interaction between the solid and the liquid phases agrees with the observed facts.

Finally it must be mentioned that the Harkins hypothesis does not agree with the results of my observations concerning the permeability of clays. An increase in pressure at constant temperature produces a *decrease* in the viscosity of water, while the results of my permeability tests clearly indicate that the viscosity rapidly *increases* with increasing density of the porous body, as soon as the diameter of the voids becomes smaller than about 100 μ .

Since on the other hand, Harkins' experiments have conclusively demonstrated that the adsorption process is associated with an important increase in density of the liquid phase, we are obliged to search for another explanation of the phenomenon.

The "Adsorbed Layer" as a Zone of Forced Vibrations.

According to the kinetic theory of heat developed by Debye, Karmán and Born, the internal energy of a substance, at a given temperature, can be represented by a vibration-spectrum. The density of the lines of this spectrum indicates the frequency of the different types of vibrations. The solid and liquid phases of gels represent two substances which, at equal temperatures, undoubtedly have funda-

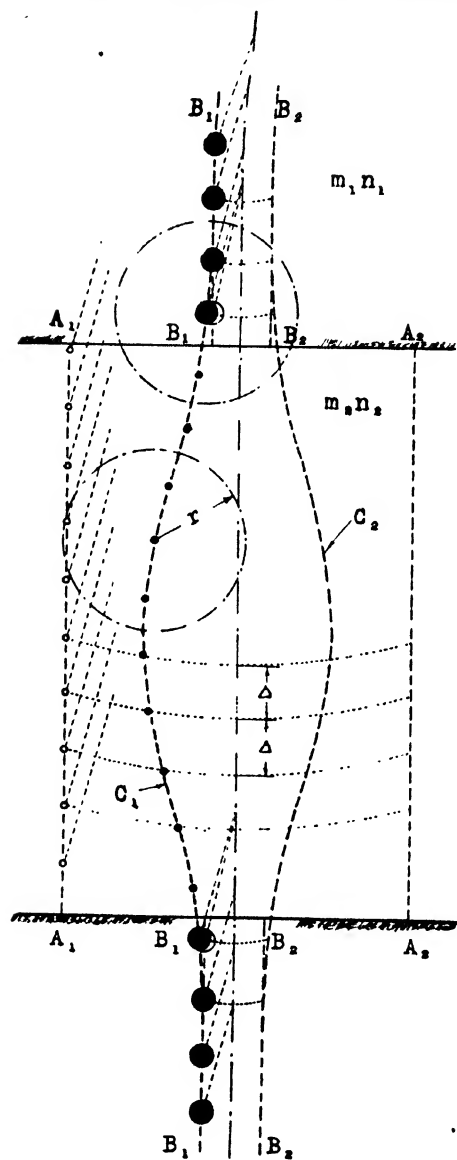


FIG. 4.

mentally different vibration spectra. However, at the boundary, the two substances are chained together by mutual molecular attraction, i.e., at least one layer of molecules of the liquid is forced to vibrate more or less in harmony with the solid. The effect thereof on the state of vibration of the liquid phase cannot yet be analyzed mathematically. However, its nature can be explained by means of the analogy represented in Figure 4. This figure shows three series of pendulums. Each pendulum of the two outer sets is supposed to have a mass m_1 and a number of oscillations n_1 . The corresponding data for the pendulums of the middle set are m_2 and n_2 . It is in addition assumed that each one of the swinging mass points strongly attracts all the other ones if they are located within a circle with a radius r . This radius corresponds to the range of molecular attraction. The distance between the paths of the oscillating points represents the average distance between the molecules. In their totality, the three systems of pendulums represent a crude analogy to a layer of liquid with a thickness d , enclosed between two solids.

Let us suppose first, that each one of the three sets of pendulums would be independent of the other ones, i.e., that there be no attraction between the mass points m_1 and m_2 , while the attraction of the mass points among the members of each group subsists. This assumption corresponds to the case, that the liquid does not wet the solid. If we simultaneously impart to each one of the masses a definite amount of kinetic energy, the members of each series of pendulums will perform simultaneous and identical oscillations, in spite of their mutual attraction. The oscillations of the mass points m_1 would be limited by the straight lines B_1B_1 and B_2B_2 respectively, those of the mass points m_2 by the straight lines A_1A_1 and A_2A_2 respectively. Hence if the liquid does not wet the solid we would predict that the presence of the solid phase would produce neither a marked change in density nor in viscosity of the liquid phase.

However, if the liquid wets the solid, i.e., if the mass points m_2 attracted not only each other but also the mass points m_1 , this attraction will influence the oscillations of the pendulums of the middle set over a range many times greater than the radius r of molecular attraction and the oscillations of the mass points of the middle set will be confined to the space located between the two dotted curves C_1 and C_2 , Figure 4.

In a two phase system in which the liquid wets the solid, the molecules of the liquid correspond to the mass points m_2 in Figure 4, tending to move at a given temperature through far wider spaces than the molecules of the solid at the same temperature. Hence the disturbing effect of the solid phase should be similar to the one produced by lowering the temperature, i.e., of *undercooling* the liquid.

Consequent upon the phenomenon thus described, the density of the liquid increases, in harmony with Harkins' results, over a layer many times thicker than the range of molecular attraction of the molecules of the solid. Mechanically, this liquid can be in a state of tension, which agrees with the results of the vapor pressure observations. And the viscosity of the liquid would be considerably greater than the normal viscosity. Let

τ_0 be the normal viscosity of the liquid at a temperature t_0 , at a pressure p_0 and at a specific volume of the liquid V_0 ,

τ the viscosity of the liquid at a specific volume $V < V_0$, at a temperature t_0 and at a pressure $p > p_0$, and

τ' the viscosity of the liquid at a specific volume $V < V_0$, at a temperature $t < t_0$ and at a pressure p_0 .

If the decrease of the specific volume of the liquid from V_0 down to V was due to increasing the pressure (first case, viscosity τ), the viscosity would be

$$\tau = \tau_0 \times (1 - 170 \cdot 10^{-6} p), \text{ which } < \tau_0$$

If on the other hand, the specific volume was decreased by undercooling the liquid, as we assume (second case, viscosity τ'), the viscosity would be

$$\tau' = 7.338 \times \frac{390 - t}{t + 28.616}, \text{ which } > \tau_0$$

rapidly increasing with decreasing temperature.

Hence the conception of the adsorbed layer as a layer of forced vibrations, with a molecular structure similar to the one of an undercooled liquid, seems thus far to agree with all the observed facts.

Vapor Pressure, Heat of Swelling and Free Energy of Gels.

If a dry gel adsorbs a quantity of 1 gram of water per 1 gram of dry matter, a quantity H of heat is liberated. This quantity shall be called the "integral heat of swelling." According to Katz⁹ the relation between i and H can be expressed by the empirical formula

$$H = \frac{A}{B + i}, \text{ where } A \text{ and } B \text{ are constants characteristic for the gel.}$$

The first derivative of H :

$$w = \frac{AB}{(B + i)^2}$$

is called the "differential heat of swelling" and indicates the quantity

⁹ *Kolloidchem. Beihfte*, **10**, 1-182 (1918).

of heat which is developed if a gel with a water content i adsorbs 1 gram of water. Let

h_1 and h_2 be the vapor pressures of a gel with water contents of i_1 and i_2 respectively,

τ_1 and τ_2 the differential heat of swelling of the same gel, at a water content of i_1 and i_2 respectively,

M the molecular weight of the liquid phase,

V_0 the specific volume of the liquid phase,

T the absolute temperature, and

R the gas constant.

If the water content of the gel increases from i_1 to i_2 by swelling without the free expansion of the gel being restricted, the quantity of heat liberated must be equal to the change in energy of the system, or

$$\tau_1 - \tau_2 = - \frac{RT}{MV_0} \ln \frac{h_1}{h_2}. \quad (8)$$

If the gel merely represented a compressible capillary system (compressible body with macro-pores), the change in energy expressed by formula (8) could be demonstrated by using the model Figure 5. This figure shows a system of compressible capillary tubes, with water contents i_1 and i_2 per gram of solid. The vapor pressures corresponding to the water contents i_1 and i_2 are determined by the curvature of the menisci, i.e., by the tension in the water, and are called h_1 and h_2 respectively. The right hand side of equation (8) represents, according to formula (3), the difference $P_1 - P_2$ of the tensions acting in the capillary water of the systems I and II. These tensions could be measured by using the Ödometer method. This method simply consists in introducing the system into the Ödometer cell, immersing the cell in water, and measuring the pressure exerted by the gel.

On the other hand, if the system be allowed to expand freely, while passing from the state I into the state II, the water is soaked into the capillary tubes on account of the elastic expansion of the tubes. In a similar manner a sponge takes up water if it is allowed to expand in a vessel filled with water. The work performed during the process of expansion is completely converted into heat, provided the tubes are so narrow that the flow proceeds slowly. Otherwise, part of the energy will be converted into elastic vibrations. If we admit to the system Figure 5 a quantity of water of 1 gram while it is in the states I and II respectively, without interfering with free expansion, the energy of expansion turned into heat due to liquid friction is, according to the laws of hydrodynamics, equal to P_1 and P_2

respectively. Hence, the difference in internal energy corresponding to the states I and II of the system is equal to

$$P_1 - P_2,$$

which in turn is equal to the change in free energy of the system. Due to this fact, the internal energy can be converted wholly into

MECHANICS OF ADSORPTION

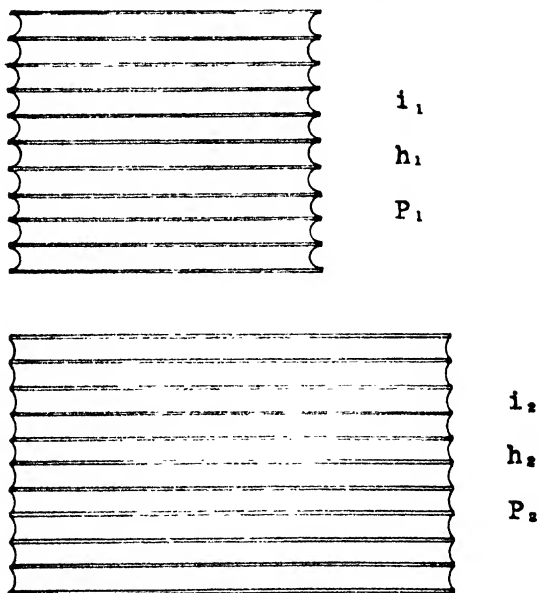


FIG. 5

external work. In practice, this conversion could be performed by artificially reducing the speed of expansion, that means by restricting the free expansion by an external pressure P_1' somewhat smaller than the swelling pressure. The lower the speed of expansion, the smaller is the amount of energy used up by liquid friction and the balance performs external work against the pressure P_1' .

As a matter of fact, according to the figures published by Freundlich¹⁰ the agreement between the values obtained by Calorimeter tests and the corresponding values computed from the results of vapor pres-

¹⁰ "Kapillarchemie" (2), 939 (1922), Table 17.8.

sure observations by means of formula (1) is quite remarkable. Even more surprising is the following fact: the heat of swelling of a system of the type shown in Figure 5 has nothing whatsoever to do with the interaction between the liquid and the solid *within* the system. The acting forces are strictly confined to the boundary between the free surface of the water and the solid phase, i.e., to the external surface formed by the menisci, and the heat of swelling of such a system is merely due to liquid friction associated with the flow. In spite of this, there exists, according to Katz,¹¹ an almost constant relation between the heat of swelling and the volume contraction of the system, the latter being exclusively due to molecular interaction *within* the system. In addition to this, it was found that the relation between the heat of swelling and the water content of a gel is almost the same as the one which exists between the water content of liquids such as H_2SO_4 and others, and the corresponding heat of mixing. In other words, there exists an intimate physico-chemical relationship between gels and solutions, a relationship which cannot possibly be accounted for by the factors which determine the heat of swelling of the capillary system Figure 5.

This relationship would remain utterly incomprehensive if the swelling pressures of gels measured by the Ödometer method were really identical with those computed by means of the vapor pressure formula (1). However, Figure 1 has suggested already, that these pressures may be very different and that they follow different laws. This discrepancy has a singular significance, if compared with the results of certain of my own tests performed with coarse grained sands, by using a method which in every respect corresponds to the Ödometer method for measuring the swelling pressure of gels. The sand, confined within a steel ring, was first put under pressure. Then the pressure was gradually released. By plotting graphically the results of the observations, curves which represented the relation between the pressure Q and the corresponding expansion e of the sand were obtained. From these curves I derived the empirical relationship

$$\frac{de}{dQ} = -A \frac{1}{e}. \quad (9)^{12}$$

In this formula e denotes the ratio between the volume of the voids and the volume occupied by the grains (voids ratio); A is a constant, whose value ranges between the limits 0.0057 and 0.01, depending on the nature of the sand. The ratio $\frac{de}{dQ}$ represents the reciprocal value of the modulus of elasticity at lateral confinement.

¹¹ *Kolloidchem. Beihefte*, 10, 1-162 (1918).

¹² Terzaghi, *Erdbaumechanik*. Wien (1925).

On the other hand, by analyzing the results of many Ödometer tests, H. Freundlich and E. Posnjak derived the empirical formula (2):

$$Q = Q_0 e^k$$

wherein e indicates the concentration of the gel (grams of dry matter per 1000 cc. of dry matter + liquid); Q_0 and k are constants. Between the concentration e and the voids ratio v , exists the relation

$$e = \frac{1000s}{1+e},$$

wherein s = specific gravity of the dry gel. Hence

$$Q = Q_0 \times 1000^k \times s^k \times \frac{1}{(1+e)^k}$$

and

$$\frac{de}{dQ} = -\frac{1+e}{k} \frac{1}{Q}. \quad (10)$$

The coefficient k in formula (9) corresponds to the coefficient $\frac{1+e}{k}$ in formula (10) and its value indicates the relative intensity of expansion at a given pressure. For sand this value varied from 0.0057 to 0.01, and for clays it ranged between 0.019 and 0.045 (very fat clays). The value of $\frac{1}{k}$ for Posnjak's elastic gels ranged between 0.242 and 0.402. On account of the small intensity of swelling of the soils which I have investigated, the value $1+e$ changed very little during the process of expansion. For this reason, and in addition on account of the importance of the hysteresis effects associated with the swelling of soils, the effect of e on the value of $\frac{de}{dQ}$ was smaller than the possible error of observation, and escaped being noticed. Hence, there seems to be little doubt about the identity of the terms (9) and (10). Formula (9) corresponds to Hooke's law for solid bodies and describes the *elastic properties of accumulations of grains*. For this reason it seems that Freundlich's formula (2) merely expresses the elastic properties of the solid phase of the gels, a property which is wholly independent of the molecular interaction between the liquid and solid phases. If one could succeed in freeing the solid phase completely from every trace of adsorbed material, without a simultaneous shrinkage of the gel, the elastic properties of the skeleton thus obtained should conform to the formula (10). The only reason

why this test cannot be realized in practice is because of the impossibility of completely evaporating the water contained in micropores.

Thus the cause of the discrepancy between the results of the Õdometer tests and those furnished by the vapor pressure formula seems gradually to emerge from the facts. It seems that the lowering of the vapor pressure is due not to a single cause, but to two essentially different causes:

- (A) the tension P'' in the liquid, and
- (B) a change P''' in the molecular energy of the liquid, or that

$$-\frac{RT}{Ml'_0} \ln h = P'' + P'''. \quad (11)$$

The part P'' corresponds to the capillary (macromechanical) part of the swelling process. According to formula (3) it is due to the tension in the liquid and produces the swelling pressure measured by the Õdometer, after the cell is immersed in the water, which reduces the tension in the water to zero. This swelling pressure is merely due to the elastic expansion of the solid phase, previously held under compression by the surface tension of the water. This purely mechanical swelling pressure represents the "free energy" of the system and can be entirely converted into mechanical work. The heat developed in connection with a change in free energy with unrestricted expansion is exclusively due to liquid friction associated with the flow of water from the surface towards the interior, while the gel expands.

The part P''' of the total energy corresponds to the molecular-mechanical part of the adsorption process. A change $P'''_1 - P'''_2$ indicates a change in the internal energy of the liquid which enters the gel, while the gel passes from a state I into a state II . This change is apparently due to the free vibrations of the molecules of the liquid being reduced to forced ones with a considerably smaller intensity. Since $P'''_1 - P'''_2$ is due to a change in the *dissipated* energy of the liquid phase, it can neither be converted into external work nor can it be detected by means of an Õdometer test. It can merely be deduced from the results of vapor pressure observations or computed from the measured value of the heat of swelling.

Thus, we are led to suspect that the process of adsorption represents the combined result of two essentially different processes: A macromechanical one, representing the manifestation of the free energy of the system, governed by the laws of ordinary capillary action, and a molecular-mechanical one, disclosing the dissipated energy of the system, governed by the laws of molecular interaction. Figure 6 represents this conception graphically, on an exaggerated scale. In this diagram the ordinates represent the water content i in grams per gram

of dry gel. The abscissæ of the curve C' represent the pressures determined by Freundlich's formula (2), which can be measured by means of an *ö*dometer, and those of the curve C the pressures computed from the results of vapor pressure observations. At high water contents the voids of the gel are wide. The space occupied by the "layers of forced vibrations" are negligible if compared with the total

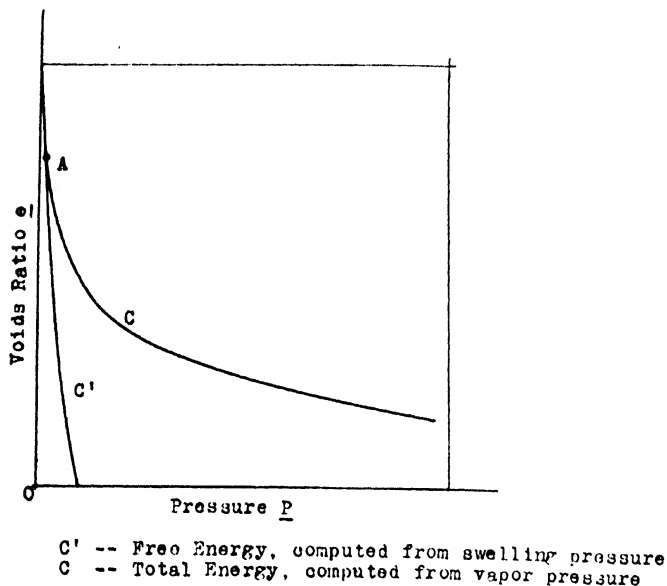


FIG. 6

volume of the liquid and, as a consequence, the quantity P'' in formula (11) is negligible if compared with P' . Hence the upper parts of the curves C' and C in Figure 6 are practically identical, and the properties of the gels are governed by the laws of ordinary capillary action. On the other hand, at high concentration of the gel, P'' becomes negligible if compared with P'' . The heat of swelling, at such concentrations, is almost exclusively due not to liquid friction, but to a change in molecular energy, which in turn shows itself in a change in density of the liquid. This seems to be the reason of the close relationship between the properties of concentrated gels and of solutions.

For the purpose of checking the conceptions presented in this paper, tests are being made by the author in cooperation with the department

of Chemical Engineering of the Massachusetts Institute of Technology. Thus far the tests have furnished the following results concerning gelatine: Freundlich's equation (2) describes the relation between the concentration and the swelling pressure with great accuracy up to the maximum swelling pressure measured with the Ödometer (52 kg. per cm.²). Under a pressure of 52 kg. per cm.² exerted by the piston of the Ödometer, the concentration of the gelatine was 850. For concentrations of 980 and 1010 the swelling pressures should be, according to Freundlich's formula, equal to 95 and 110 kg. per cm.² respectively. The vapor pressure formula furnished, for the same concentrations, the values 222 and 450 kg. per cm.². Hence the term (10) would be, for these two concentrations, $P' + P'' = 95 + 127$ and $110 + 340$, respectively. The tests are still being continued.

Analogy Between Gels and Solutions.

Let H be the heat in calories, liberated, if a dry gel adsorbs i gram of water per gram of dry matter, or if 1 gram of a pure liquid (H_2SO_4 , etc.) is mixed with i gram of water per gram of solvent, and C the volume contraction in cc. associated with these processes.

According to Katz, the value of the ratio $\frac{C}{H}$ ranges between the following limits:

$$\text{For gels} \quad \frac{C}{H} = 10 \text{ to } 32 \times 10^{-4}.$$

$$\text{For true solutions,} \quad \frac{C}{H} = 11 \text{ to } 25 \times 10^{-4}.$$

The close agreement between these values is obvious, and considering the fact that they refer to two fundamentally different systems, certainly is striking. However, it seems to be explained by the assumption expressed by formula (11) and by what is shown in Figure 6. Neither the heat of swelling nor the volume contraction can be determined except for gels with a high concentration, because at low concentrations these quantities are too small to be measured. At high concentrations, P' in formula (11) (the mechanical part of the cause of the lowering of the vapor pressure) becomes negligible if compared with P'' . P'' , the factor which expresses the change in the molecular state of the adsorbed liquid, dominates, and this factor is physically identical with what causes the lowering of the vapor pressure and the heat of mixing for solutions.

This analogy calls our attention to another relation which seems to

exist between gels and solutions, i.e., the relation between the swelling pressure and the osmotic pressure. Let

h and h_1 be the vapor pressure of the pure liquid and of the solution respectively,

V_0 the specific volume of the solution,

M the molecular weight,

T the absolute temperature of the solution,

R the gas constant, and

P the osmotic pressure.

Between these quantities exists the known relation

$$P = \frac{RT}{MV_0} \ln \frac{h}{h_1} \quad (12)$$

This equation is identical with the equation (1), that means, if P in equation (1) were identical with the swelling pressure measured with the Ödometer, osmotic pressure and swelling pressure should be identical. It is surprising to notice that the identity of these formulas was known; the essential difference which exists between the osmotic pressure and the swelling pressure was also known. Nevertheless, it was believed that P in formula (1) represented the swelling pressure.

If we apply to the case of the osmotic pressure the conception presented in this paper concerning the physical character of the adsorption process, we would have to give to the facts the following interpretation:

In the general equation (11)

$$-\frac{RT}{MV_0} \ln h = P' + P''$$

P' is the swelling pressure which represents the equivalent of the tension in the liquid, produced by the surface tension at the boundary gas-liquid-solid. P'' represents the change in internal energy. The smaller the voids, the smaller is P' in comparison with P'' . For true solutions P' becomes equal to zero, because due to the absence of voids no more capillary phenomena exist, and P'' represents the osmotic pressure, while the swelling pressure P' strictly follows the law of the compression of coarse mechanical capillary systems. *The swelling pressure P' as measured by the Ödometer method seems to have nothing in common with the molecular part of the adsorption phenomenon.*

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SPECIFIC ION EFFECTS IN THE BEHAVIOR OF TANNING AGENTS TOWARD COLLAGEN TREATED WITH NEUTRAL SALTS

By K. H. GUSTAVSON

The action of neutral salts upon proteins is a problem of great physiological importance and our knowledge in this field has been largely enriched by the physiological chemists. This question has also an important practical application in the manufacture of leather, particularly in the preparation of skins for tanning. This investigation deals with the behavior of the hide protein, collagen, treated with equimolar solutions of neutral salts toward the most important classes of tanning agents, the vegetable tannins and the chromium and aluminum salts.

Hofmeister's¹ classical researches in regard to the swelling and coagulating effects of a number of inorganic salts upon several proteins originated the well known ion series bearing his name. He found that the relative effectiveness of the salts in these respects could be arranged in nearly the same order for the several proteins investigated. The anions formed the series: sulfate, citrate, tartrate, chloride, chlorate, nitrate, bromide, iodide, and thiocyanate, where the coagulating effect decreases with descendance of the series but the swelling and peptization increase in the above order. These observations apply only to a neutral or slightly alkaline reaction of the proteins and their solutions as it was found later that the order is reversed in acidic medium.² Later, several workers, foremost among them Wolfgang Pauli,³ have confirmed these findings. The reversal of the anion series brought about by a change in reaction served to indicate that the experimental conditions were of great significance for the behavior of the protein and the controlling factors of pH and of the purity of the protein have now long been established. It was therefore near to hand to suspect that the Hofmeister series were only fictitious and produced by lack of control of these factors, the importance of which was not realized at the time of the pioneering investigations. Loeb⁴ in his well known and elaborate investigations came to the conclusion that the

¹ *Pflüger's Arch.*, 24, 247 (1888); 25, 1 (1889); 27, 395 (1890); 28, 210 (1891).

² Posternak, *Ann. de l'Institut Pasteur*, 15, 85 (1901); cited from Freundlich's "Kapillar chemie."

³ Pauli, *Pflüger's Arch.*, 71, 333 (1908); *Heitr. physiol. path. Chem.*, 3, 225 (1903).

⁴ "Proteins and the Theory of Colloidal Behavior," 65-111 (1922).

Hofmeister series is not valid but that the so-called lyotropic effect is produced by the change in pH by the added salts. No specific ion effect was noticeable at constant pH values for isoelectric protein as material in case of salts of the same valency type. His observations were readily explained from the ionic concept of protein reactions and by the application of the Donnan membrane equilibrium to protein systems, as first pointed out by Procter and Wilson⁵ in their classical researches of the acid-gelatin equilibrium. The action of neutral salts upon protein solutions and proteins in the isoelectric state in regard to coagulation and peptization, could however not be explained by "the concept of colloidal behavior" and Loeb admitted that in this case, the determining factor is probably an indirect effect due to secondary valency action between protein and solvent.

Loeb's categorical denial of the existence of a specific ion effect in general has been criticized as his observations were carried out in dilute solutions where the effect of H- and OH-ions predominates and where the result therefore will be according to the valency rule. Such a dual nature of the action of neutral salt has been amply illustrated by Michaelis,⁶ who found that the flocculating effect of neutral salts upon serum albumin increases in order: $\text{CNS} > \text{I} > \text{Br} > \text{Cl} > \text{SO}_4$, in salt concentrations from 0.1 to 0.5 normal. This order is reversed in higher concentrations than one-normal and the sulfate shows now the greatest flocculating power. Similar results were obtained in a study of the swelling of agar as influenced by neutral salts, where the lyotropic nature was evident only in high salt concentrations. Michaelis considers that the neutral salt action in dilute solutions is largely due to electro-static influence of the adsorbed ions, where accordingly, the sign of charge and the valency rule will be the governing factors. The lyotropic nature of the salt solutions is however more prominent in high concentrations, possibly due to a competition of the salt and the hydrophilic colloid for water.

A satisfactory explanation of the neutral salt effect has however not yet been advanced and the final answer will probably not be given before the problem of activation of neutral salts in concentrated solution and our knowledge of the structure of proteins have been further advanced. The important investigations carried out by Stiasny⁷ and his pupils showed that the change in dispersity of gelatin solution by neutral salts, employing ashfree isoelectric material at a constant pH, follows the lyotropic series. The peptization of proteins by means of neutral salts has been explained by Hardy⁸ as a primary valency compound formation, the salt radicals combined with the nitrogenous

⁵ Procter, *J. Chem. Soc.*, 105, 313 (1914); Procter and Wilson, *ibid.*, 109, 307 (1916).

⁶ "The Effect of Ions in Colloidal Systems," 82-103 (1925).

⁷ Stiasny and Das Gupta, *Colloquium*, 13 (1925); Stiasny, Das Gupta, and Tresser, *ibid.*, 23 (1925); *Kolloid-Z.*, 35, 853 (1924).

⁸ *J. Physiol.*, 33, 251 (1905).

groups. This view can, however, not be upheld in the light of Pfeiffer's⁹ systematic work in regard to the neutral salt compounds with amino acids, polypeptides, and piperazines, which researches have clearly demonstrated the failure of the classic valency theory in this instance and they have instead definitely established the formed addition compounds to be of secondary valency nature.

Thomas and Foster¹⁰ have contributed to the problem here in question in their study of the behavior of hide substance, in the form of hide powder, toward neutral halides and sulfates. The neutral halides were found to exert a destructive action upon hide powder, where, on the other hand sulfates were effective hide preservatives. The order of cations and anions were, in a general way, in concordance with the Hofmeister series.

An explanation of this problem, based upon the modern concept of the structure of proteins and Pfeiffer's previously mentioned fundamental researches seems at the present to be most serviceable. The view of proteins as long-chained polypeptide structures of an extremely high molecular weight as promulgated by Emil Fischer's classical investigations has during the recent years been replaced by the concept of protein as consisting of simpler units of relatively low molecular weight, held together to a supermolecular structure by secondary valency, cohesion or similar forces. The organochemical view was inadequate in explaining the action of protease and a number of colloidal reactions. This new school of protein chemistry, whose advancement is intimately connected with the names of Stransky, Herzog, Abderhalden and Bergmann, has received important experimental substantiations by the X-ray diffraction diagram of proteins, the molecular weight determinations of the same in phenol and particularly by Bergmann's¹¹ synthesis of protein-like compounds from unsaturated diketo-piperazines, exhibiting marked affinity for tanning agents and dyestuffs, besides possessing the regular protein characteristics. The elementary cell of collagen from the X-ray diagram is reported by Herzog and Gonnell¹² to indicate a molecular weight of not more than 685, which value shows an excellent agreement with that of 750 deduced by Wilson¹³ from the data on the acid-gelatin system. These units form the colloidal micelle of a considerable "molecular weight."

Pfeiffer has prepared in crystalline form, a number of definite molecular compounds between halides and protein-prototypes, which physicochemical measurements showed to exist as complexes also in solution. The stability of these complexes followed in a general way

⁹ "Organische Molekülverbindungen." Stuttgart, 106-124 (1923); where complete literature references are given also.

¹⁰ *J. Ind. Eng. Chem.*, 17, 1162 (1925).

¹¹ *Naturwissenschaften*, 13, 1045 (1925).

¹² *Ber.*, 58B, 2228 (1925).

¹³ *Wilson, J. Am. Leather Chem. Assoc.*, 12, 108 (1917).

the Hofmeister series. The great tendency of halides to form such addition compounds by means of residual valency is probably one of the most important factors in the peptization of proteins and similar aggregated substances by salts. The internal forces between the protein constituents are weakened by the partition of secondary valency forces to the neutral salt and a partial breaking up of the structure is the result. Sulfates do not form any such compounds and their action seems rather to be of the reverse nature tending to increase these internal forces, associating the ultimate units, as judged from the behavior of hide substance treated with neutral sulfates toward certain tanning agents. Michaelis has found that neutral salt can displace the isoelectric point, which evidently shows that the same is not controlled only by the acidic and basic dissociation constants of the protein. The great divergency in reported isoelectric points of several proteins, e.g., gelatin and collagen, is also probably due to such secondary valency effect influenced by the previous history of the protein (chiefly alkaline and acid treatments) as evident from the work of Wo. Ostwald and his collaborators¹⁴ on gelatin. The neutral salt treatment of gelatin is not connected with any change in primary valency function of the gelatin as the primary amino-groups are left intact which is evidenced by the Sørensen formol value and the Van Slyke number remaining the same.¹⁵ From data to be presented in this paper, it is also indicated that the pretreatment with neutral salts does not involve primary valency forces, as the fixations of acids and alkalis by the various hide powder specimens were independent of the salt treatment. It is thus possible to prepare by treatment of hide substance with neutral salt, series of proteins of different degree of aggregation. The behavior of such treated hide substance toward tanning agents is expected to contribute to our knowledge of the theory of tanning. In light of the above considerations, the reactivity of a protein may be due to (1) primary valency action of the elementary units, (2) secondary valency, as corresponding to coordination compounds, (3) residual valency without any such numerical characteristics, to which cohesive forces also belong, corresponding to Langmuir's and Haber's conception of adsorption. Any sharp demarcation between the three types can, however, not be drawn at the present status of the nature of valency and atomic structure. The neutral salt treatment does not concern the first category but changes in the second and third factors are produced. It is therefore expected that where a reaction by primary valency takes place the extent of combination must be independent of any such pretreatment, and, on the other hand, it is expected that a combination of tanning agents with hide substance by means of sec-

¹⁴ Ostwald, Kuhn, and Bohme, *Kolloidchem. Beihefte*, 20, 412 (1925).

¹⁵ Stianzy, Das Gupta, and Tresser, *Collegium*, 24 (1925).

ondary valency or surface forces will be controlled by the state of the hide powder in regard to its degree of aggregation, specific surface and secondary valency capacity.

Experimental.

100 gram portions of collagen in form of Standard Hide Powder was treated with one liter of molar solutions of a number of neutral salts for 14 days at room temperature (20-22° C.). The salts were of C. P. grade and their pH values in the concentration used were in the range of 5.6 to 6.0. A layer of toluene served to check any biochemical action taking place. The treated hide powders were washed free from salts, dehydrated with 96 per cent alcohol and air-dried. The dry hide powder was then analyzed for moisture, ash and collagen. The ash content of the neutral salt treated hide powders did not in any instance appreciably exceed the value found for the blank, treated with water, which indicated a thorough washing of the hide powders. The amount of peptized hide substance was determined in the filtered solution by the Kjeldahl method and includes products of widely different dispersities. Table I contains the percentages of peptized hide substance on the total amount of protein. The portions of hide powder soaked in solutions of CaCl_2 , BaCl_2 , KI and KCNS were in the wet state very sticky and showed after drying a blackish appearance. The destructive action was in these instances very pronounced.

TABLE I
PEPTIZATION OF HIDE POWDER BY NEUTRAL SALTS
(14 days treatment)

Nature of Salt Solution	Per Cent Loss of Hide Substance
M Na_2SO_4	1.8
" $\text{Na}_2\text{S}_2\text{O}_3$	1.2
" MgSO_4	1.6
0.5 M K_2SO_4	3.8
H_2O	4.9
M NaCl	7.8
" KCl	7.0
" MgCl_2	9.3
" KBr	14.4
" KI	16.8
" BaCl_2	14.8
" SrCl_2	21.1
" KCNS	24.2
" CaCl_2	31.9

Increasing peptization for cations: $\text{Ca} > \text{Sr} > \text{Ba} > \text{Mg} > \text{Na}, \text{K}$.

Increasing peptization for anions: $\text{CNS} > \text{I} > \text{Br} > \text{Cl} > \text{SO}_4, \text{S}_2\text{O}_3$.

Portions of hide powder equal to 3.00 grams of collagen were weighed into 500 cc. shaking bottles and 50 cc. H_2O was added to secure complete hydration. An accurately measured volume of solutions of tanning agent, generally in 200 cc. portions, was added after 6 hours soaking of hide powder and the bottles rotated for 48 hours at 20-21° C. The vegetable tanned hide powder was washed with distilled water until negative gelatin-salt test for tannin and negative ferric chloride test for non-tannins were obtained and then dried. Analysis of moisture, ash and collagen was carried out for the vegetable tanned stock. The difference was taken as irreversibly combined tannin and the amount of the same combined with 100 grams of collagen stated. The amounts of Cr_2O_3 and collagen were determined in the chrome tanned product. The amount of Cr_2O_3 fixed by hide substance is given in terms of grams Cr_2O_3 combined with 100 grams of collagen. The H-ion concentration of the original solutions was ascertained electrometrically and these determinations also carried out in the solutions after finished interaction, where this was possible. Cathaphoresis observations were carried out in a modified Michaelis apparatus employing M KCl solution.

RESULTS

I. The Acid Binding Capacity.

Portions of hide powder equal to 1.80 grams collagen were treated under continuous shaking with 200 cc. portions of 0.01 N H_2SO_4 for 24 hours. Equilibrium was established within this time. The pH values of the equilibrium solutions were determined.

TABLE II

Hide Powder Treated with	pH at Equilibrium
H_2O	2.62
M Na_2SO_4	2.62
" KCl	2.62
" KBr	2.62
" KNO_3	2.62
" KCNS	2.62
" KI	2.62
" SrCl_2	2.62
" CaCl_2	2.62

pH of 0.01 N H_2SO_4 2.06

The same specimens of hide powder showed identical fixative capacity, as measured by pH of external solution at equilibrium, in series with 0.1 N H_2SO_4 and 0.01 N NaOH.

II. Vegetable Tanning.

The use of hide powder without any previous soaking was found unsatisfactory. Rather strong tannin solutions had to be employed to secure an excess of tannin in the exhaust and overtanning of the surface of the dry hide powder occurred. This was particularly noticeable for the hide powders treated with solutions of CaCl_2 , SrCl_2 , BaCl_2 , KI and KCNS . Even when hydrated hide powder was employed in these instances a partial overtanning of the surface was evident and the values of the fixed tannins are therefore only semi-quantitative. The

TABLE III
HEMLOCK EXTRACT

45.0 grams per liter total solids. pH of original solution: 4.10.

Hide Powder Treated with	pH of Exhaust	Grams Tannin Combined with 100
		Grams Collagen
M Na_2SO_4	4.40	40.1
" MgSO_4	4.40	42.1
" $(\text{NH}_4)_2\text{SO}_4$	4.41	49.8
0.5 M K_2SO_4	4.41	51.6
" H_2O	4.42	56.8
M NaCl	4.43	62.0
" KCl	4.43	62.2
" KNO_3	4.43	59.3
0.5 M KClO_3	4.43	61.6
M MgCl_2	4.44	63.2
" KBr	4.44	65.4
" KI	4.46	73.8
" KCNS	80.4
" SrCl_2	4.48	76.6
" BaCl_2	4.48	80.3
" CaCl_2	4.48	78.9

TABLE IV
HEMLOCK EXTRACT

22.5 grams per liter total solids (at pH 4.20).

Hide Powder Treated with	Grams Tannin Fixed by 100 Grams Collagen			
	at pH 2.40	at pH 4.20	at pH 7.15	at pH 8.20
M Na_2SO_4	40.2	30.1	38.6	14.9
" H_2O	49.7	40.2	48.6	21.0
M NaCl	50.2	41.6	50.4	28.2
" KCl	49.8	41.2	50.0	24.6
" KBr	54.0	44.1	51.6	27.5
" KI	59.2	45.2	59.2	30.9
" KCNS	61.2	44.8	60.4	31.8
" BaCl_2	58.7	47.0	58.2	31.5
" CaCl_2	58.4	47.8	60.8	32.8

tannin extracts employed were those of hemlock, sulfited quebracho and sumac. The findings were similar for all specimens and the data from the hemlock series are therefore only reported as the most extensive investigation was carried out with this extract.

The stock solution was decanted and filtered to remove the coarse suspended matter. The amount of total solids was determined in the original solution. Adjustment to different pH values was done by addition of N HCl and NaOH.

In some preliminary experiments, the hide powder in 50 gram portions was soaked with 500 cc. of salt solutions and 0.2 cc. 40 per cent formaldehyde added to prevent putrefaction. Such treated hide powder gave on the whole the same series as here described, but a noteworthy exception in results was found for the Na_2SO_4 -treated stock, which gave only about a third of the tannin fixation found for the blank. The values for fixed chromium in the chrome experiments with the hide powder treated with neutral sulfates were also considerably lower than those obtained by the toluene-preserved hide powder.

III. Chrome Tanning.

The basic sulfates and chlorides of chromium are the principal tanning agents employed in the manufacture of chrome leather. The composition of these compounds is here stated in the per cent acidity, i.e., the per cent of chromium combined with hydrolyzable acidic groups on the total amount of chromium. In practice, acidities from 50 to 70 per cent are mostly encountered. Chromium exists in these salts principally as a positively charged complex and in the liquors here examined only a slight anodic migration was observed in solutions of acidities from about 50 to 60 per cent immediately after preparation, but the same ceased upon standing. The extremely basic salts (40-45 per cent acid) exhibited a very pronounced anodic migration, of about the same magnitude as that of the cathodic, immediately after preparation. The amount of electro-negative complexes decreased, however, very considerably upon standing in this case also, and after 3 to 4 weeks was hardly noticeable. More recent investigations have shown that certain negatively charged complexes possess a pronounced tanning action and it has been indicated that the reaction between anodic chromium and collagen is of definitely different character than the cathodic chrome tanning process.¹⁶ Sodium-oxalato-chromate and sulfito-compounds were therefore studied in order to test this assertion. Chromium is present entirely in anodic form in both of these compounds. The question of the hydration of the hide powder is not

¹⁶ Gustavson, *J. Am. Leather Chem. Assoc.*, **21**, 22 (1926).

of the same significance in these series as in the vegetable tanning, and any overtanning does not occur with use of dry hide powder except for extremely basic sulfate. The use of dry hide powder is therefore justified.

TABLE V

40.6 PER CENT ACID CHROME LIQUOR

(Prepared by neutralization of a 63 per cent acid chromic sulfate with NaHCO_3 .)
Concentration: 15.4 grams Cr_2O_3 per liter. Diluted to this concentration immediately before the start of experiment. Cataphoresis: cathodic and anodic of about equal magnitude (2 grams hydrated hide powder* and 200 cc. of solution).

Hide Powder Treated with		pH of Final Exhaust	Grams Cr_2O_3 Combined with 100 Grams Collagen
M	Na_2SO_4	3.32	18.24
"	$\text{Na}_2\text{S}_2\text{O}_3$	3.34	21.02
0.5 M	KClO_3	3.34	22.13
	H_2O	3.35	23.68
M	NH_4Cl	3.34	23.82
"	KCl	3.34	24.05
"	NaCl	3.35	24.22
"	MgCl_2	3.35	24.96
"	KBr	3.36	26.45
"	KI	3.37	30.84
"	KCNS	3.39	32.16
"	SrCl_2	3.36	27.12
"	BaCl_2	3.36	28.30
"	CaCl_2	3.37	29.84

* All weights of hide powders given in the tables are on collagen basis.

TABLE VI

45.8 PER CENT ACID CHROME LIQUOR

(Prepared by adding NaHCO_3 to a 63 per cent acid chromic sulfate.) Concentration: 11.8 grams Cr_2O_3 per liter. Diluted to this concentration immediately before use. Considerable anodic migration. (2 grams dry hide powder + 200 cc. solution)

Hide Powder Treated with		Grams Cr_2O_3 Combined with 100 Grams Collagen
M	Na_2SO_4	15.14
	H_2O	18.00
M	KCl	18.42
"	NaCl	18.23
"	MgCl_2	18.61
"	KBr	19.48
"	KI	21.26
"	KCNS	23.64
"	SrCl_2	20.76
"	BaCl_2	21.11
"	CaCl_2	22.46

TABLE VII

THE SAME LIQUOR BUT FOUR WEEKS OLD SOLUTION

Solution exhibited only a slight anodic migration. (2 grams of dry hide powder + 200 cc. solution.)

Hide Powder Treated with	Grams Cr_2O_3 Combined with 100 Grams of Collagen
M Na_2SO_4	20.02
H_2O	20.37
M NaCl	20.36
" MgCl_2	20.41
" KBr	20.32
" KI	20.16
" KCNS	20.08
" SrCl_2	20.32
" BaCl_2	20.15
" CaCl_2	20.02

The same liquor diluted immediately before use was also employed on hydrated hide powder and very similar differences in tanning fixation by various hide powders as reported in Table VI were obtained, which evidently shows that the results obtained are not due to the *modus operandi* employed.

TABLE VIII

63 PER CENT ACID CHROME LIQUOR

Concentration: 14.0 grams Cr_2O_3 per liter. Immediately diluted to this concentration before tanning. Only cathodic migration. (3 grams of hydrated hide powder + 200 cc. solution.)

Hide Powder Treated with	pH of Final Exhaust	Grams Cr_2O_3 Combined with 100 Grams Collagen
M Na_2SO_4	2.95	11.43
H_2O	2.95	11.56
M NaCl	2.95	11.52
" KCl	2.95	11.58
" KBr	2.95	11.46
" KI	2.95	11.23
" KCNS	2.94	11.30
" SrCl_2	2.95	11.52
" BaCl_2	2.94	11.36
" CaCl_2	2.94	11.19

Similar results were obtained by a five-weeks' old solution, employing dry hide powder.

The pure cathodic migration of the liquid used in the experiment cited in Table VIII was changed into a partial anodic by making the solution one-molar in Na_2SO_4 . The behavior of this liquor towards the highly peptized hide powders was now similar to that of the extremely basic freshly prepared liquors, showing a relatively increased chrome fixation, compared to the blank, for the deaggregated hide powders.

SPECIFICATION EFFECTS

TABLE IX

A 63 per cent Acid Chrome Liquor was diluted immediately before the start of the experiment to contain 14.0 grams Cr_2O_3 per liter and Na_2SO_4 added to give one-molar concentration. 2 grams dry hide powder + 200 cc. solution. Cathodic and anodic migration. Time: 28 hours.

Hide Powder Treated with		Per Cent Cr_2O_3 on Dry Basis
	H_2O	2.00
M	Na_2SO_4	2.06
"	KBr	2.27
"	KCNS	2.58
"	SrCl_2	2.42
"	CaCl_2	2.64

TABLE X

92 PER CENT ACID CHROMIC SULFATE

Concentration: 13.1 grams Cr_2O_3 per liter. Cathodic migration.
(2 grams of dry hide powder + 200 cc. solution.)

Hide Powder Treated with		pH of Final Exhaust	Grams Cr_2O_3 Combined with 100 Grams Collagen
M	Na_2SO_4	2.06	2.97
	H_2O	2.06	3.02
M	NaCl	2.06	2.98
"	KI	2.06	2.93
"	KCNS	2.06	2.98
"	BaCl_2	2.06	3.04
"	CaCl_2	2.06	2.96

The basic chromic chlorides have little tendency compared with sulfates to complex formation. A 69.8 per cent acid chromic chloride was investigated.

TABLE XI

69.8 PER CENT ACID CHROMIC CHLORIDE

Concentration: 12.95 grams Cr_2O_3 per liter. Cathodic migration.
(5 grams dry hide powder + 200 cc. solution.)

Hide Powder Treated with		pH of Final Exhaust	Grams Cr_2O_3 Combined with 100 Grams Collagen
M	Na_2SO_4	2.69	5.08
	H_2O	2.69	5.16
M	NaCl	2.69	5.13
"	KCNS	2.69	5.23
"	BaCl_2	2.69	5.16
"	CaCl_2	2.69	5.10

The anodic chrome tanning agent sodium-oxalato-chromate, in solutions containing about 10 grams Cr_2O_3 per liter, possesses its greatest combining capacity with hide powder in the isoelectric range of collagen (pH 5.0-5.5).¹⁷ This interesting finding indicates the secondary valency nature of this reaction.

¹⁷ Gustavson, *loc. cit.*

TABLE XII

ANODIC SODIUM-OXALATO-CHROMIATE

Solutions were 6 months old and with established pH equilibrium. Concentration: 12.5 grams Cr_2O_3 per liter. pH of original solution: 4.97. Anodic migration. (2 grams of collagen as dry hide powder and 200 cc. solution.)

Hide Powder Treated with		pH of Final Solution	Grams Cr_2O_3 Combined with 100 Grams Collagen
M	Na_2SO_4	5.06	6.72
	H_2O	5.07	7.02
M	KCl	5.07	7.18
"	KBr	5.07	7.36
"	KI	5.08	7.69
"	KCNS	5.08	8.75
"	BaCl_2	5.07	7.80
"	CaCl_2	5.08	8.19

TABLE XIII

ANODIC SULFITE-COMPOUND

Concentration: 11.3 grams Cr_2O_3 per liter, containing 3 Na_2SO_3 ; 1 Cr_2O_3 ; pH value 4.8.* Anodic migration. (2 grams dry hide powder + 200 cc. solution.)

Hide Powder Treated with		Grams Cr_2O_3 Combined with 100 Grams Collagen
M	Na_2SO_4	16.84
0.5 M	K_2SO_4	18.96
	H_2O	20.83
M	NaCl	21.32
"	KCl	21.48
"	KBr	23.70
"	KI	25.96
"	KCNS	31.28
0.5 M	$\text{K}_4(\text{CN})_6\text{Fe}$..	22.45
M	KNO_3	22.68
"	SrCl_2	26.30
"	BaCl_2	28.44
"	CaCl_2	30.62

* The highest potential immediately set up was taken and corresponds to this pH value. The quinhydrone electrode gave a pH value of 4.9.

Stiasny¹⁸ has investigated the tanning action of chromic sulfates (chrome liquors) containing increasing amounts of sodium sulfite. He found that by this addition a gradual increase in the amount of electro-negative chrome complexes occurs and the chrome fixation is also increased to a certain limit. This maximum is located where the proportion of 3 Na_2SO_3 to 1 Cr_2O_3 is reached, and under these conditions the migration is entirely anodic. Na_2SO_3 was added in this proportion to the 63 per cent acid liquor which was thereafter diluted to contain 11.3 grams Cr_2O_3 per liter. Solutions were "aged" for two

¹⁸ *Collegium*, 41 (1926).

weeks. The molecular-dispersed form of the original solution was by this addition transferred into a partially colloidal solution. This was evidenced by the gradually developed turbidity upon standing.

An extremely basic sulfite-compound was prepared by pipetting 100 cc. of a 34 per cent acid chrome liquor (prepared by adding NaHCO_3 to the 63 per cent acid stock liquor) in a concentration of 226.0 grams Cr_2O_3 per liter into a solution of 113 grams $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, diluting to 2 liters. A very viscous solution resulted.

TABLE XIV

2 grams hydrated hide powder + 200 cc. of above solution.

Time: 48 hours.

Hide Powder Treated with	Grams Cr_2O_3 Combined with 100 Grams Collagen
H_2O	2.63
M Na_2SO_4	2.39
" KCNS	3.67
" CaCl_2	3.48

A number of experiments were also performed with hydrated hide powder, treated exactly the same as in the reported experiments, with the exception of omitting the alcoholic dehydration. The results from these series were similar to those here reported.

Alum Tannage.

Sodium bicarbonate was added to a highly concentrated aluminum sulfate solution to form a salt corresponding in composition to $\text{Al}_2(\text{OH})_2(\text{SO}_4)_2\text{Na}_2\text{SO}_4$. The resulting concentration was 30.0 grams Al_2O_3 per liter. This solution was aged 10 weeks before use.

TABLE XV

Two grams hide powder were soaked with 50 cc. water for 6 hours. A quantity of 50 cc. of 66 per cent acid aluminum sulfate, 30 g/l Al_2O_3 , was thereafter added. Time: 28 hours. pH of original solution (30.0 g/l Al_2O_3) 3.55. pH of solution immediately after dilution (15.0 g/l Al_2O_3) 3.62.

Hide Powder Treated with	pH of Exhaust	Grams Al_2O_3 Combined with 100 Grams Collagen
H_2O	3.72	6.67
M Na_2SO_4	3.72	6.16
" KCl	3.72	6.89
" KBr	3.72	7.09
" KI	3.73	7.85
" KCNS	3.73	8.14
" SrCl_2	3.72	7.87
" CaCl_2	3.72	8.15

DISCUSSION OF RESULTS

The Dispergation of Hide Powder by Neutral Salts.

The relative dispergating capacity of neutral salts upon hide powder gives series which are practically identical with the Hofmeister's. This widely different influence of neutral salts here found is not due to variation in pH, as the H-ion concentration was as constant as can be expected in this pH region without use of any buffers, the use of which was, of course, out of the question. The different degree of peptization by the various neutral salts is instead a manifestation of specific ionic effects. Pfeiffer has shown that the increase in solubility of isoelectric glycine in neutral salt solutions follows a similar order, where the degree of stability of the formed secondary valency complex determines the solubility. The dispergation of hide substance may therefore in part safely be considered due to a breaking up of the protein aggregate into micelles, probably also leading to products of greater dispersity, by formation of such addition compounds between salts and degradation products or weakening of the intermolecular and intermicellar forces. Similar lyotropic effects have been reported by von Weimarn¹⁹ in regard to the dispergating influence of neutral salts upon cellulose and the order found was identical with that here observed. A similar explanation of this action may apply to cellulose and other aggregated structures.

The reaction mechanism between acids and alkalies on the one hand and proteins on the other seems at the present to be in general firmly established as a salt formation of stoichiometric nature and the formed protein compound might preferably be considered as an ammonium salt in accordance with Werner's theory. Simultaneously occurring colloidal changes, e.g., of dispersity and degree of aggregation must, however, also be considered. That the stability of the internal structure of the protein is affected by primary and possibly also by secondary valency reactions is not unexpected from the aggregation viewpoint of protein structure. In the pH range from 2.5 to 10.5, this salt formation is accounted for by union taking place by means of the amino and carboxyl groups of the protein. Hoffman and Gortner²⁰ found in their extensive investigations of 14 different proteins in this respect that the quantity of acid and alkali bound by the protein in this range is controlled by the chemical nature of the protein. The ionic view is therefore justified in this instance. The peptide-linkage is probably involved at higher pH values. At extremely low and

¹⁹ Von Weimarn and collaborators, Reports of the Imp. Ind. Research Institute, Osaka, Japan, 8, No. 10, 11-67, from *Chem. Abstracts*, 20, 818 (1926).

²⁰ *Colloid Symposium Monograph*, 2, 209-368 (1924).

high pH values it was found by these workers that the binding capacities of the different proteins were the same, regardless of their chemical composition. An adsorption mechanism was therefore made probably under these conditions. The acid and alkali binding capacities of the hide powder specimens treated with neutral salts are found to be independent of their degree of aggregation. The method employed is not strictly quantitative but the best available, as a direct determination of the protein-salt compound cannot be carried out on account of the three phase nature of this system and the instability of the formed compound. The method employed is, however, in this case accurate enough to establish that adsorption forces of physical nature do not partake to any considerable extent in this reaction, in view of the very pronounced differences in combining rate found for constituents of colloidal character.

Vegetable Tannage.

The fixation of vegetable tannin by neutral salt treated hide powders at the same pH and identical experimental conditions shows the following order of increase. Anions: $\text{CNS} > \text{I} > \text{Br} > \text{Cl} > \text{H}_2\text{O} > \text{SO}_4$, and the cations form the series: $\text{Ca} > \text{Ba} > \text{Sr} > \text{Mg} > \text{K}$, Na. The same order is obtained in a pH range from 2.2 to 8.2. It has previously been noted that great difficulty was encountered in securing a uniform tannin fixation of the hide powder exhibiting the greatest peptization, even in a perfectly hydrated state. This surface overtanning ("case hardening") is due to the increase rate of combination caused, in its order, by the increase in specific surface and intermolecular forces by the salt treatment, and the surface layer acts as a screen for the diffusion of tannins. Therefore, it is not possible to draw any definite conclusion in regard to any particular pH-range or concentration of extract where the change in fixation, due to the changed nature of the hide powder, is most pronounced. The difference between the blank and the hide powders exhibiting slight increase is too uncertain to serve for this purpose.

A number of theories have been advanced to account for the mechanism of the vegetable tannage. The only theory, however, which has reached a state where the speculative element is largely eliminated and to which is applicable quantitative treatment, is that promulgated by Procter and Wilson.²¹ This theory is based upon the conception of the ampholytic nature of collagen and the application of the Donnan membrane equilibrium to behavior of proteins. The potential difference set up by the unequal distribution of ions in the gel and the bulk of solution is governed by the pH, if other factors

²¹ *J. Am. Leather Chem. Assoc.*, **12**, 76 (1917); *J. Chem. Soc.*, **100**, 1327 (1916).

are kept constant. A minimum potential is located at the isoelectric point of the hide protein and the charge increases with decrease in pH until a maximum is reached at a pH of about 2. The tannins are negatively charged in this H-ion range and the tanning process, to its nature a mutual co-precipitation of two oppositely charged systems, is to its extent controlled by the sum of the absolute values of these potentials. The Procter-Wilson theory explains rationally the degree of tannin fixation as a function of H-ion concentration in this range and also the action of added substances upon the same property. Thomas and Kelly²² found, however, in one of their important investigations in this field that a considerable tanning action also is evident on the alkaline side of the isoelectric point, exhibiting a maximum at a pH of about 7. This fixation was not expected from the view of Procter and Wilson but the finding of Wilson and Kern²³ of a second isoelectric point in the vicinity of pH 7.6 was considered to account for this additional range of tanning. The existence of this second isoelectric point is not yet definitely established and it has been considered that the same is fictitious, due to a buffer action.²⁴ In case the existence of two isoelectric points is true, the question is still open if they are caused by intermolecular rearrangement by change in pH or if collagen consists of two different proteins. Several facts indicate, however, that the Procter and Wilson theory does not include all factors, which control the rate and nature of the vegetable tanning process. Thomas and Kelly²⁵ found that a considerable tannin fixation occurs at lower pH than 2 and greater than 7.6 where tannin and collagen possess charges of equal sign. This finding is not clear from the electro-neutralization standpoint. They also demonstrated that the hide powders tanned in solutions of pH > 5.0 are more resistant to the action of alcohol than those tanned in solutions of lower pH range.²⁶ Foster²⁷ found that deaminized hide powder shows an increased rate of tannin fixation in the alkaline range with reference to the isoelectric point, compared to regular hide powder where, on the other hand, in the acid range the reverse is true. The concept of Procter and Wilson must therefore probably be supplemented by other factors. The wide difference in fixation of tannin, which in some instances takes such a considerable proportion as over 100 per cent and which is very likely caused by changes in specific surface and intermolecular forces, leaves ample evidence that the vegetable tanning process is not as simple as would follow from the ionic theory of Procter and Wilson. The order of tannin fixation is

²² *J. Ind. Eng. Chem.*, 15, 1148 (1923).

²³ *J. Am. Chem. Soc.*, 44, 2633 (1922); see also Thomas and Kelly, *ibid.*, 47, 833 (1925).

²⁴ Atkin and Douglass, *J. Soc. Leather Trades' Chem.*, 8, 359 (1924).

²⁵ *J. Ind. Eng. Chem.*, 15, 1148 (1923).

²⁶ Thomas and Kelly, *J. Ind. Eng. Chem.*, 16, 81 (1924).

²⁷ "The Behavior of Deaminized Collagen" Dissertation, Columbia University, New York City (1925); Thomas and Foster, *J. Am. Chem. Soc.*, 48, 489 (1926).

the same as found in the peptization series by the neutral salts. From the theory of Procter and Wilson the same rate of tannin fixation would follow, if the pH and other factors of the solution are kept constant.

The slight difference in pH of the final solution after interaction is due to the different degree of fixation of tannin and cannot explain the wide difference in fixed tannin found. Two other reactions are probably going on simultaneously with the co-precipitation process (1) the increased surface action will increase fixation of colloidal constituents, (2) phenolic bodies of high dispersity react to form molecular compounds by means of the strongly induced secondary valency field. The first factor is expected to be more pronounced at lower pH and with increase in concentration of the tannin solution as the colloidal of tannin is here greater than in the alkaline range where phenolic bodies and also quinone-like structures are preponderant. The formation of molecular and chemical compounds must therefore be given more importance at higher pH values. No definite conclusion in regard to the relative proportions of these three factors can be derived from the present data, for reasons previously pointed out. Moreover, the present status of our knowledge of valency and colloidal phenomena does not permit the drawing of any sharp demarcation between these three, hypothetically advanced, processes. The following conclusion is, however, with safety permissible: The vegetable tannage cannot solely be elucidated as an electro deposition process but secondary valency and specific surface forces play also a prominent rôle. The substantial evidences of the chemical nature of the vegetable tanning, accumulated by Thomas and his collaborators in their studies of collagen and structurally changed collagen towards tannins, cannot be disregarded. The same applies to the types of reaction here treated. The final solution of this problem must consider all these factors.

Chrome Tannage.

In light of the very intricate nature of the components in the one-bath chrome tanning process, it is not surprising to find that no one theory has met with approval by the many contributors to this field. From the one extreme of considering the chrome fixation as a surface coating of colloidal chromic oxide to the other extreme, postulating this final compound as formed by a regular salt formation in accordance with the stoichiometric law, are to be found a whole range of speculations and hypotheses, mostly derived from very incomplete and unsatisfactory data. The colloidal view, advancing the co-precipitation of the two oppositely charged systems of col-

lagen and colloidal chromic hydroxide, has not taken into consideration that chrome tanning is carried out in an acidic medium, and where also the components are both positively charged. The excellent tanning action of chromium compounds of pure crystalloid nature evidently shows that the colloidal state of the tanning agent is not a criterion of a mineral tanning agent. The origin of this view goes back to investigations of the behavior of gelatin and the findings have been transferred to explain the tanning of collagen without any experimental evidence being offered for this particular case. This explanation has lately been revived by Wintgen²⁸ who has in a series of investigations of chromium hydroxide sols added greatly to our knowledge of the stability of complex colloid cations as a function of the composition of the inter-micellar solution, and their precipitation of gelatin. These last investigations, however, have lost in value by lack of pH control. Stiasny,²⁹ to whom we are indebted for the first rational treatise of the chrome tanning process and also for more recent important contributions in this field, has in his more recent work stressed the importance of the Werner concept as applied to chrome leather problems. The criterion of a mineral tanning agent is, according to Stiasny, the presence of replaceable aquo-groups in the coordinative sphere, whereby a secondary valency action is secured, and further the presence of basic groups (hydroxo) which serve to facilitate condensation reactions, leading to products of semi-colloidal or colloidal dispersities. According to Stiasny, the mechanism of tanning consists in the formation of molecular compounds probably through basic groups of the protein; and also, subsequent colloidal changes of the formed complex probably play an important rôle. Thomas and Wilson³⁰ interpret their researches in which the importance of physico-chemical methods and technic applied to leather problems has been particularly emphasized, as indicating the formation of primary valency compounds termed chromium-collagenates. This view of collagen acting as an anion on the acid side of the isoelectric point would seem at first to be contrary to Loch's finding of the reactivity of proteins, but a slight activation of collagen as an acid in this pH range seems reasonable in light of the Bjerrum³¹ theory for the constitution of ampholytes, and the great insolubility of the formed chromium-collagen-compound explains the gradual fixation of chromium. The objection raised against Wintgen's view is not here justified as the constitutional factor, and not the charge of the micelles of the protein is concerned as in the colloidal hypothesis. An inter-

²⁸ *Collegium*, Nos 656, 657 (1925), where literature references are given also.

²⁹ *Collegium*, 327 (1908); 126 (1909); 95, 113 (1923); *Z. anorg. Chem.*, 37, 918 (1924); Stiasny, Lochmann, and Mezzy, *Collegium*, 190 (1925); Stiasny and Lochmann, *ibid.*, 200 (1925).

³⁰ See Wilson, "The Chemistry of Leather Manufacture," 278-308 (1923).

³¹ Bjerrum, *Z. physik. Chem.*, 104, 147 (1923).

mediate hypothesis of chrome tanning as of dual nature, has received considerable experimental support.³² The fixation of cathodic chromium by collagen is considered to be an internal complex salt formation, in which primary valency is concerned. The reaction mechanism of anodic chromium, the tanning action of which Stiasny and the writer have investigated, is best classified as a secondary valency complex formation. The partition of secondary valency by the basic groups of the protein is probably also a very important factor in the fixation of chromium cations. The reactivity of the acidic groups of the protein is induced by disturbance of the valency field, causing an activation of the protein. A number of experimental findings have demonstrated that a profound difference in nature of cathodic and anodic chromium fixation really exists and the behavior of certain complexes (oxalato) shows a close parallelism to the vegetable tannins, which also probably react chiefly with the basic groups of the collagen. That, however, a primary valency function is not required in chrome tanning is evident from the maximum chromium fixation from this oxalato-compound occurring in the pH range 5.0-5.5, the isoelectric zone, which finding besides a number of others cannot be reconciled with the concept of chrome tanning as a purely primary valency reaction in all cases. The final product was as perfectly tanned as the cathodic chrome tanned hide powder as measured by the water resistance test.

The present investigation brings out exactly the same difference in nature of the two classes of chrome compounds. Independence of any salt pretreatment of the hide powder is shown in the chrome fixation by the various hide powders from solutions, which show cathodic migration of chromium entirely. Extremely basic sulfates exhibit immediately after dilution, a very considerable anodic migration, in many instances of the same magnitude as that of the cathodic, but upon standing these negatively charged complexes are broken down and after 3 to 4 weeks the anodic migration has generally ceased. The data show that in freshly prepared solutions, the combining capacity of the various hide powders is dependent upon the salt treatment and definite ion series corresponding to the Hofmeister's are evident. But the same liquor in equilibrium shows practically the same value in Cr_2O_3 for all hide powders. This was verified with dry hide powder for both series and it was found that any case-hardening does not occur as the same rate of increase is exhibited by solutions made up immediately before use both for hydrated and dry hide powder. The possibility of specific surface reactions with colloidal constituents of these basic liquors must also be considered.

The tanning action of extremely basic chromic sulfate with col-

³² Gustavson, *J. Am. Leather Chem. Assoc.*, 21, 22 (1926).

loidal characteristics and possessing both electro-positive and electro-negative chrome complexes is in all probability due to (1) Primary valency partition between chrome cation and anodic collagen, (2) Formation of molecular compounds between anodic chromium and collagen, (3) Adsorption of colloidal constituents. Ultra-filtration experiments which are planned, will probably give more information regarding the second and third factors.

Sulfito-complexes and oxalato-chromate illustrate the behavior of negatively charged chromium complexes. The anions form the series: $\text{CNS} > \text{I} > \text{Br} > \text{Cl} > \text{H}_2\text{O} > \text{SO}_4$, where the thiocyanate treated stock shows the greatest chrome fixation and the sulfate treated the smallest. The colloidal constituents of the aged sulfito-compound accentuate further the difference in obtained Cr_2O_3 -values. A very good illustration of this dual nature of chrome tanning, in regard to cathodic and anodic complexes, gives the following example:

The original 63 per cent acid chromic sulfate containing entirely chromium cations, gives the same values for Cr_2O_3 -fixation in all cases, but by addition of 3 mols Na_2SO_4 to 1 mol of Cr_2O_3 the complete formation of chrome anions is secured and the degree of dispersity is decreased and now the fixation depends upon the nature of the hide powder in regard to its secondary valency action and specific surface forces. The pH value of the sulfito-compound, 4.8, is in the isoelectric zone of collagen and the very pronounced chrome fixation in this case makes probable the secondary valency nature of the process.

That the decrease in the degree of dispersity of the chromium salt caused by the addition of sulfito, is not wholly responsible for the different behavior of the two types of compounds toward the peptized hide powder, is shown by the data from the 63 per cent acid chrome liquor and the same liquor made molar in sodium sulfate. Colloidal constituents could not be detected by ultra-filtration through collodion membranes in any of these solutions. The partial formation of chrome anions by the increase in SO_4 -anions³³ must therefore be the underlying cause of the different rate of chrome fixation by the series of deaggregated hide powders. The same reasoning applies to the anodic oxalato-solution.

Our present knowledge of the possible reactions between chromium compounds and collagen may be summarized as:

(1) Ionic reaction of cathodic chromium or chromium complexes. This primary valency reaction likely involves the acidic protein groups (carboxyl) and the result is an internal complex compound.

(2) Secondary valency reaction of anodic chromium complexes by means of the basic protein groups. The formed chrome-collagen.

³³ Gustavson, *Collegium*, 97 (1926).

complex is in type similar to the Werner inorganic ammin-compounds.

(3) Colloidal constituents are fixed by means of specific surface forces.

The view that cathodic chrome fixation (the regular one-bath chrome tanning) of its nature is radically different from the other types of tannage, is supported, among many other facts, by the behavior of differently tanned hide powders to the tryptic digestion. The regularly chrome tanned hide powder resists this action, where, on the other hand, the specimens tanned with other agents, are digested.⁸⁴

Alum Tannage.

The data from the 66 per cent acid aluminum sulfate show that the fixation of Al_2O_3 by hide powder depends upon its degree of aggregation, and the rate of Al-fixation by the neutral salt treated hide powders follows also here their degree of peptization, i.e., the Hofmeister series are applicable. The corresponding chromium salt of the same per cent acidity gives equal chrome fixation for the different specimens of hide powder. This different behavior of aluminum- and chromium-salts of corresponding per cent acidity is not unexpected as the tendency to formation of cationic micelles of considerable aggregation ("colloidal ions") and electro-negative complexes is very much more pronounced for the former.⁴⁵ Alum tannage, with experimental conditions similar to those in the cited experiment, involves likely all these factors of reactivity, thus showing a parallel to the tanning mechanism of extremely basic freshly prepared chrome liquors.

The importance of the degree of peptization of the hide powder in reactions with tanning agents of colloidal and secondary valency nature has been further demonstrated by investigations, not yet published, where a pretreatment of the hide powder with acid and alkaline solutions and subsequent transference of such treated hide powder to the isoelectric state was carried out. It was found in an investigation of the behavior of formaldehyde treated hide powder toward tanning agents that the pH of the solution, in which this pretanning was carried out, radically influences the capacity of the final isoelectric product in regard to its combination with tanning agents. The formaldehyde collagen formed at lower pH values (6–8), exhibits less capacity and rate of combination with tanning agents where, on the other hand, the hide powder, treated with formaldehyde at higher pH values (> 12)

⁸⁴ Seymour-Jones, "The Hydrolysis of Collagen by Trypsin," Dissertation, Columbia (1923), 17-23; Thomas and Seymour-Jones, *J. Ind. Eng. Chem.*, **16**, 157 (1924).

⁴⁵ Pauli, *Kolloid-Z.*, **28**, 4 (1921).

has in general greater affinity for tanning agents. These findings focused the attention upon the changes in degree of aggregation of the hide protein taking place with the formation of the collagen-salt. The data from the afore-mentioned series with pretreatment at different pH values further substantiate the views here presented.

Summary.

(1) The dispergation of hide powder by neutral salt solutions in molar concentrations at the same pH and with other experimental conditions the same, exhibits specific ion effects. The Hofmeister series is shown to be valid.

(2) The fixation of acids and alkalies is independent of the degree of aggregation of the neutral salt treated collagen.

(3) The combination of vegetable tannin with collagen under the same experimental conditions is largely a function of the state of the hide powder in regard to its secondary valency activity and specific surface forces. The vegetable tannage cannot be explained simply as an electro-neutralization process. The Procter-Wilson concept of this process must be supplemented by other factors. The formation of secondary valency and adsorption compounds is made probable. Hide powder treated with neutral sulfates shows diminished capacity of tannin fixation. Neutral halide treatment of the hide powder leads to an increased rate of combination with tannin. The order of fixation by the different specimens is identical to the Hofmeister series.

(4) This investigation adds further support to the view of the one bath chrome tanning process as carried out in practice, as being essentially a reaction involving primary valency. Cathodic chromium, in the form of chlorides and sulfates, gives practically the same chrome fixation for all specimens of hide powder, independent of its previous history.

(5) The anodic chromium compounds, of oxalato- and sulfito-type have been investigated. Their reactivity with collagen is a function of its degree of aggregation, and the order of increase of the fixed Cr_2O_3 is represented by the Hofmeister series. The colloidal nature of certain negative complexes is probably a supplementary factor in this mode of tanning. The secondary valency nature of the anodic chrome fixation is made probable and the view of the dual nature of the chrome tanning process has received further substantiation.

(6) Extremely basic sulfate liquors in freshly prepared state exhibit also specific ion effects in their reactions with neutral salt treated

collagen. In this instance, the reaction mechanism may be considered to be due to

(a) A primary valency reaction between chrome complexes or positively charged micelles and the carboxyl group of the protein.

(b) Formation of molecular compounds by means of the basic protein groups with the complex chromium anions.

(c) Processes of pure "adsorptive nature" controlled by the specific surface potential of the hide powder.

(7) Basic aluminum sulfate, in its rate of combination with skin protein, is controlled by the state of the same. The mechanism of this reaction seems to be similar to that of the extremely basic sulfate liquors. Primary and secondary valency forces together with adsorptive forces probably occur simultaneously.

(8) Pretreatment of hide powder with acids and alkalis affects the reactivity of the hide powder in a very similar manner to that found in the treatment with neutral halides.

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OBSERVATIONS OF THE COLLOIDAL BEHAVIOR OF AQUEOUS GELATIN SYSTEMS

BY ELMER O. KRAEMER

In the face of conflicting views, opinions and hypotheses, the most certain inference to be made concerning the various interpretations of protein behavior is that they all lack an indisputable basis and complete substantiation; as a corollary, it is safe to conclude that, first, more information and data, and secondly, a more general and comprehensive viewpoint in attempting interpretations are required. It is our intention to present preliminary results which, when completed, may be found useful in obtaining a more adequate grasp than we now possess of the physico-chemical behavior of proteins and other materials deporting themselves similarly. The spirit of the studies is one of willingness to recognize the straightforward chemical features as well as those features which in general are evident in and assumed to be characteristic of polyphasic or disperse systems. In the present paper, gelatin is the subject of attention, not only since it is a typical protein, but also because of its capacity to form gels like many heterogeneous or disperse systems.

LIGHT-SCATTERING CAPACITY OF GELATIN SYSTEMS

The tyndall effect or light-scattering capacity is one of the most characteristic properties of disperse or colloid systems; studies of the tyndall effect therefore should give rather direct information concerning the strictly colloid behavior of protein systems. Two of the many variables upon which the magnitude of the tyndall effect in gelatin systems is strikingly dependent are temperature and H-ion activity (pH). The influence of these two factors upon the tyndall effects in a number of gelatin systems is discussed below.¹

De-ashed Gelatins:

In Figure 1 are shown the relationships between pH, temperature and the light-scattering capacities of 1 per cent (1 gram vacuum dried gelatin in 100 cc.) gelatin systems made up from stock de-ashed

¹ These studies were made with the cooperation of Mr. Dexter and will be published in greater detail elsewhere. The tyndall effect curve in Fig. 13 is from recent work with Mr. G. H. Joseph.

by Eastman Kodak Company. At temperatures of 40-50° C., when the gelatin is in a sol condition, the tyndall effect is not great and is almost independent of temperature and pH. A slight hump appears in the region about a pH of 5. At these temperatures, a constant intensity of scattered light is attained practically as soon as thermal equilibrium. At lower temperatures, which bring about gel formation, there suddenly appears an extremely pronounced maximum at a pH of 4.95, indicating a maximum in the precipitation tendency under

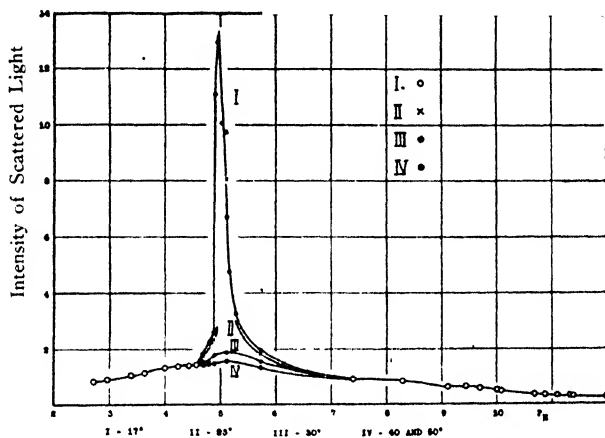


FIG. 1.—Influence of pH and temperature upon the tyndall effect of 1.0 per cent de-ashed hide gelatin systems.

these conditions. Below pH 4.5 and above pH 7.5, the curves show no change in tyndall effect as the temperature is lowered to 17° C. Without doubt, this maximum locates the isoelectric point of the gelatin in spite of the fact that pH 4.7 is usually quoted for this point.

The suddenness with which the intensity of the scattered light rises for a change in pH of a few tenths of a unit is particularly striking and noteworthy. At 17° C., the tyndall effect increases at least 400 per cent for a change of 0.03 pH (4.87-4.90). No simple relationship is revealed between this behavior and the combination of gelatin with acid or base, or the dependence of cataphoretic mobility upon pH.² In a 1 per cent gelatin system, as little as 0.001 N HCl is sufficient to remove the striking tyndall effect and the precipitation tendency by the formation of "solution units" with a low light-scattering capacity. It is commonly recognized that the ease of precipitation of

² Private communication from Dr. Veazey.

gelatin by means of alcohol similarly decreases very rapidly as one leaves the isoelectric point.

In connection with the behavior of gelatin at a pH near 8, and a possible "second isoelectric point"² it is of interest to note that a slight but distinct hump in the tyndall effect—pH curve appears at a pH ca 8 shortly after the temperature is lowered to 17° C. Upon aging, however, the tyndall effect at pH's between 5. and 8. gradually increases, leading to the disappearance of the hump. The increase in tyndall effect in the neighborhood of pH 5. may extend over considerable time, but at 17° C. the change was slight between the 24th and 75th hours.

The discrepancy in the pH of the isoelectric point given above and the value usually quoted (4.7) raises the question as to the existence of a unique molecular species which can be called gelatin. If

TABLE I
THE ISOELECTRIC POINTS OF DE-ASHED GELATINS AS DETERMINED BY THE pH OF MAXIMUM TYNDALL EFFECT

Eastman A		Eastman A'		Eastman B		Eastman C	
pH	Tyn. Eff.	pH	Tyn. Eff.	pH	Tyn. Eff.	pH	Tyn. Eff.
√4.65	1.62	4.92	13.8	4.88	4.1	4.92	13.4
4.87	2.59	√4.97	18.8	4.90	9.3	4.96	14.3
4.90	11.1	5.00	8.3	5.00	11.5	5.02	10.6
4.95	12.9			√5.03	5.9	√5.16	5.3
5.03	10.6			5.13	0.86		
5.10	9.7						
5.12	6.7						

Silver Label De-ashed		Ossein Gelatin	
pH	Tyn. Eff.	pH	Tyn. Eff.
4.90	1.96	√4.80	
4.97	10.6	4.90	0.49
√5.01	14.3	5.00	2.9
5.07	0.80	5.30	10.6
5.48	.24	5.52	13.9
		5.90	8.4
		7.25	0.34

√pH of 1 per cent system without added acid or alkali

Underscored pH defines the isoelectric point within limits of errors.

Eastman A and C were de-ashed by Eastman Kodak Company by washing and precipitation of the gelatin

Eastman B was de-ashed by electrodialysis of the molten gel by Eastman Kodak Company.

Eastman A' and Silver Label were de-ashed by Dr. Ralph Mason by electrodialysis, without membranes, of a 10 per cent gel at 5° C.

Ossein gelatin was extracted below 60° C. from purified ossein furnished by the Hammond Organic Products Co. and de-ashed by Loeb's washing method.

² Cf. Kraemer, *J. phys. Chem.*, **29**, 410 (1925) Cf. Kraemer and Fanselow, *J. phys. Chem.*, **29**, 1169 (1925).

gelatin systems contain a single chemical entity with definite properties uniquely determined by the conditions under which it exists, it should be characterized by a uniform and constant isoelectric point. The sharpness with which the maximum tyndall effect appears at the isoelectric points presents a very convenient and accurate method for determining this point. The results of the application of the method to several specimens of de-ashed gelatins are given below.

For the first five (hide) gelatins, the maximum tyndall effect—and therefore *presumably* the isoelectric point—is located at practically a constant pH (4.95-5.01) in spite of great differences in gel strength. Eastman B, for instance, behaves like a very low grade gelatin. The isoelectric point of the ossein gelatin, on the other hand, falls at pH 5.5 (the H-ion activity being less than one-third as great as at the isoelectric point of the hide gelatins). Furthermore, the maximum in the tyndall effect—pH curve is broader and flatter than in those shown by the hide gelatins.

Table I shows also that the Eastman gelatins and the ossein gelatin are not in the isoelectric condition, but contain a trace of acid or base. Removal of the excess acid or base does not change the pH of maximum tyndall effect (cf. Eastman A and A'), but tends to give rise to a still sharper maximum. The commercial Silver Label gelatin containing ash gives a maximum tyndall effect at the same pH as does the de-ashed Silver Label gelatin. Electro dialysis as a de-ashing procedure is therefore without influence upon the isoelectric point of the gelatin.

Commercial Hide and Bone Gelatins:

Since the isoelectric points of the commercial and de-ashed Silver Label gelatins are identical, it seems possible that the normal ash has a negligible influence upon the pH of maximum tyndall effect. In Figures 2, 3 and 4 are given data on the isoelectric points of various commercial gelatins. Data fixing the isoelectric points of a series of calf-skin gelatins representing successive extractions of the same raw stock are given in Figure 2. In spite of considerable differences in quality and gel strength, the isoelectric points of the members of the series fall at pH's between 4.90 and 5.00.

Figure 3 shows however that the highest grade member of a series of Delft bone gelatins behaves rather like the de-ashed ossein gelatin already described, for the maximum tyndall effect appears at pH 5.5. Succeeding members of the series show a pH for the maximum tyndall effect (and isoelectric point) shifting toward a value of 4.9. In this series, the intensity of the tyndall effect also decreases with decreasing quality of gelatin.

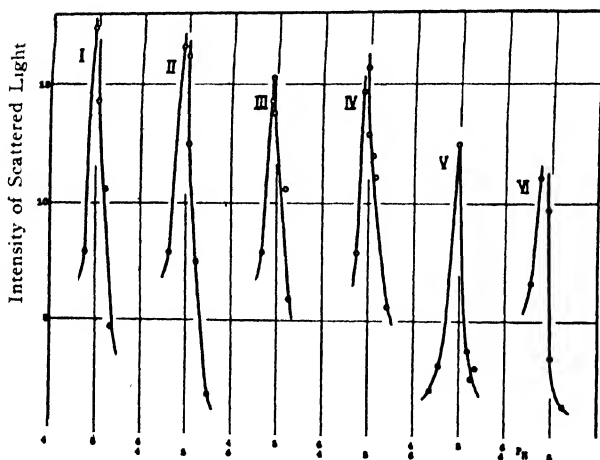


FIG. 2.—Isoelectric points of successive extractions of calfskin gelatin stock as shown by the pH of maximum tyndall effect.

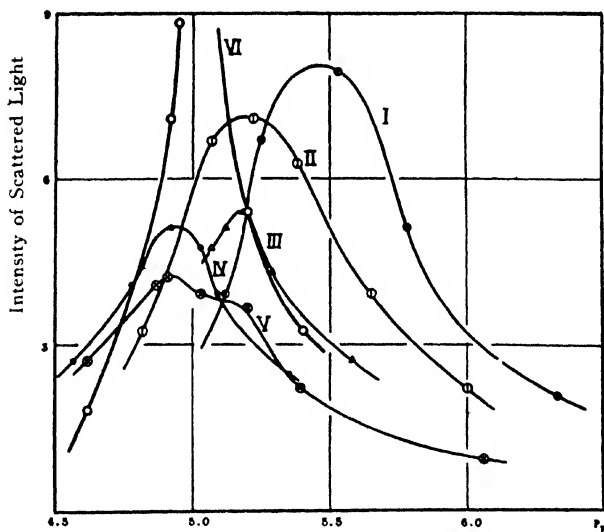


FIG. 3.—Isoelectric points of bone gels. I-V, Successive extractions of bone stock. VI, Blended bone gelatin.

In Figure 4 are given the data for the isoelectric points of various other gelatins. A third extraction (above 80° C.) of the purified ossein yielding the de-ashed ossein gelatin mentioned above, shows an isoelectric point at pH 4.85. The form of the tyndall effect—pH curve resembles those for the hide gelatins. A particularly interesting specimen is the pigskin gelatin with the isoelectric point near pH 8.

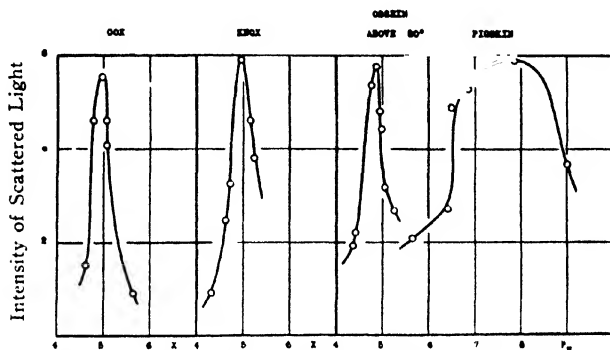


Fig. 4.—Isoelectric points of various gelatins as shown by the pH of maximum tyndall effect.

It appears, therefore, that the term "gelatin" is applied to materials differing considerably in their behavior, even with respect to a property like the isoelectric point which is usually thought to be distinctive and unique.⁴ This fluctuation in the isoelectric point suggests either that "gelatin" consists of an unknown number of unknown chemical substances or that the so-called isoelectric point of such material does not bear the relation to the chemical character of the material which is implied in the application of the theory of ampholytes to its behavior. In any case, the absence of a single demonstrable chemical entity places great difficulties in the way of interpreting the chemical and physico-chemical behavior of such substances.

Gelatin Mixtures:

It is sometimes suggested that the "second isoelectric point" of gelatin is due to the presence of an impurity the isoelectric point of which gives rise to the "second point." The possession of various gelatins with various isoelectric points makes it possible to deter-

⁴ Gerngross and Bach (*Biochem. Zeit.*, 143, 542 (1923)) have also found that the isoelectric points of various gelatins fluctuate between pH 4.5 and 5.5. For them, the higher pH's were shown by *hide* gelatins.

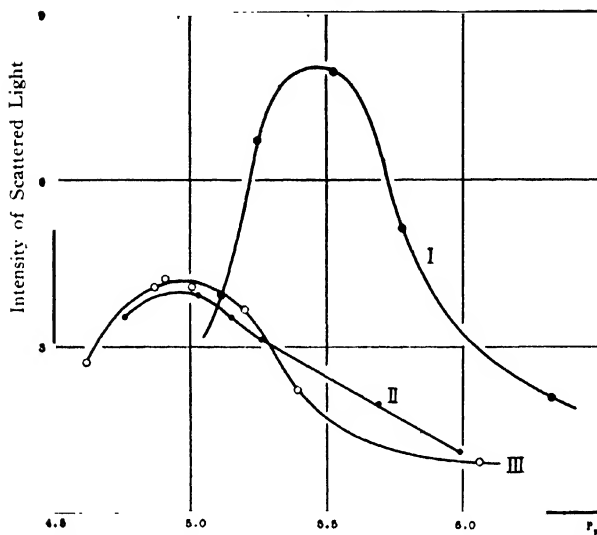


FIG. 5.—Comparison of the tyndall effects of a mixed bone gelatin with the tyndall effects of the single components.

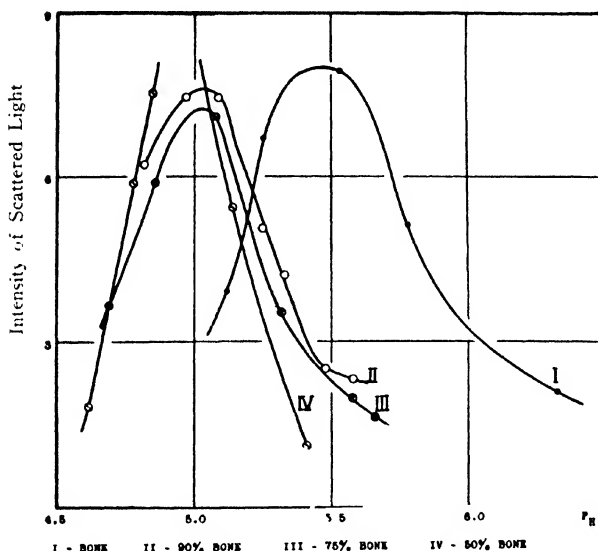


FIG. 6.—Tyndall effects in mixtures of hide and bone gelatin

mine whether such mixtures actually reveal double isoelectric points corresponding to their compositions. In Figures 5, 6 and 7 are given data for the apparent isoelectric points of various mixtures as determined by the influence of pH upon tyndall effect. It is evident that double isoelectric points do not occur. Instead, a maximum tyndall

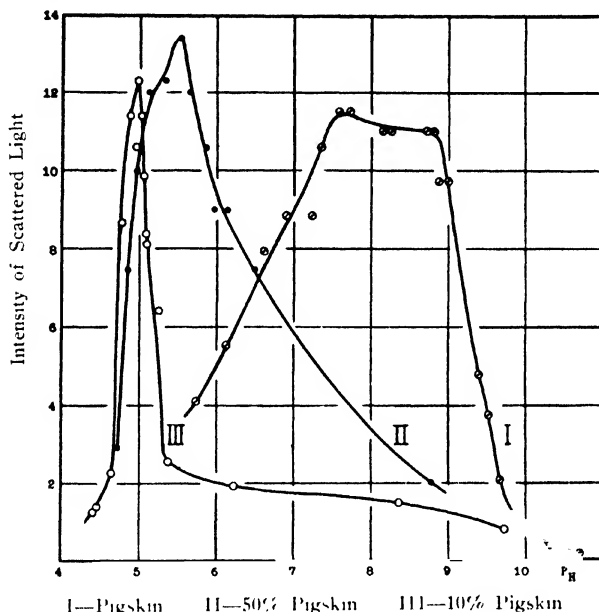


Fig. 7—Tyndall effects in mixtures of calf skin and pigskin gelatins.

effect, maximum precipitation tendency and apparent isoelectric point appear at a pH intermediate between those of the two components. In general, the component with isoelectric point near pH 5 is more effective—on the basis of relative masses—than the other component in determining the pH of the maximum for the mixture. Thus in Figure 6, the maximum tyndall effect in a mixture containing 90 per cent of bone gelatin is but slightly different from that of the other component. Mixtures of calf and pigskin gelatins behave similarly (Figure 7). Any gelatin system may likewise consist of an unknown number of components without revealing the fact in such an examination. Theoretical considerations, therefore, which are based upon the assumption of the existence of definite and uniform gelatin molecules

as units in aqueous gelatin systems would appear rather artificial and formal. This is also true of other protein systems—as of casein—which there is good reason to believe are also heterogeneous systems.⁵

OPTICAL ACTIVITY AND THE RESISTANCE-TO-SHEAR OF GELATIN SYSTEMS⁶

In connection with the tyndall effects of gelatin systems their capacity to form gels should also be considered. In general, the formation

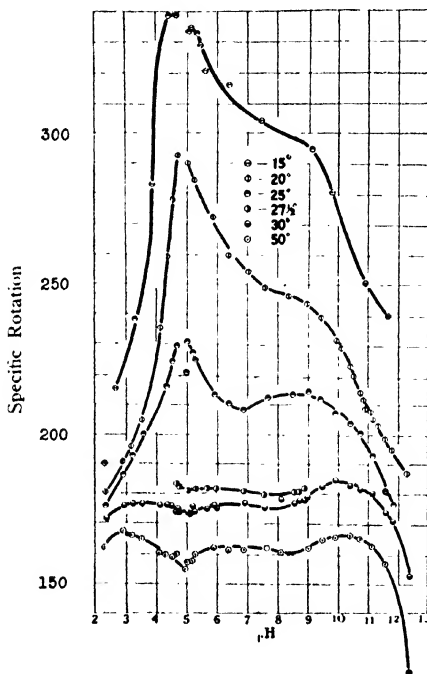


Fig. 8.—Influence of pH and temperature upon the specific rotation of 0.47 per cent gelatin systems (de-ashed). pH's adjusted with acetic acid and sodium hydroxide.

of a gel may be considered as the result of an incomplete or unsuccessful precipitation of a disperse phase from a colloid system.⁷ If

⁵ Cf. Lindstrom-Lang, *Compt. rend. trav. lab. Carlsberg*, 16 (1925).

⁶ These investigations were made with the cooperation of Mr. John R. Fanselow and will be published in greater detail elsewhere. Cf. *J. phys. Chem.*, 29, 1169 (1925).

⁷ Cf. *J. phys. Chem.*, 29, 1523 (1925).

this general view is applicable to gelatin systems, a close relationship should exist between gel formation and tyndall effects. The work of C. R. Smith⁸ has suggested that a rather intimate connection exists between the optical activity of gelatin systems and their capacity

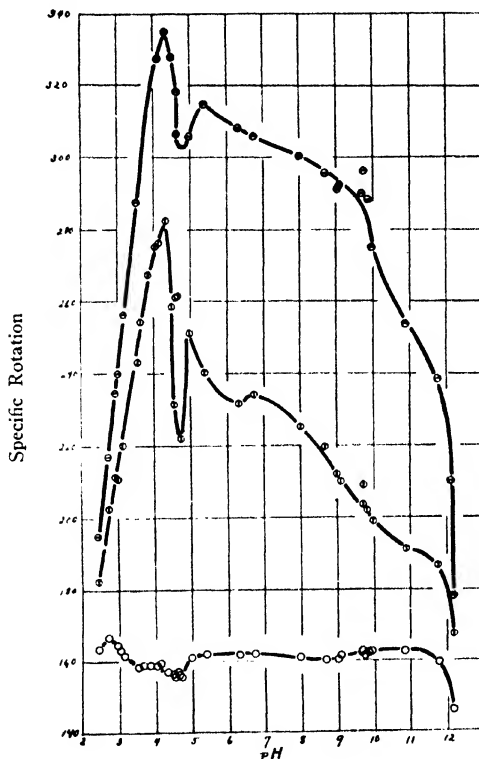


Fig. 9.—Influence of pH and temperature upon the specific rotation of 0.31 per cent gelatin systems. pH's adjusted with acetic acid and sodium hydroxide. Measurements were made through a short tube in order to obtain readings near pH. Curves are for 15°, 20° and 40° C.

to form gels, but a systematic study of the dependence of optical activity upon temperature and pH has been lacking. A comparison of the influence of pH and temperature upon the tyndall effect, optical activity and gel strength or resistance-to-shear reveals a number of interesting and surprising features.

⁸ *J. Am. Chem. Soc.*, **41**, 185 (1919).

In Figure 8 may be seen a graphical presentation of the relationships between temperature, pH and optical activity of 0.47 per cent de-aired gelatin systems, the pH's being adjusted by the use of acetic acid and sodium hydroxide. Depending upon the temperature, the curves show one of two forms. At $27\frac{1}{2}^{\circ}\text{C}$. or higher, there is a minimum specific rotation at pH 5 and pH 8-9, but no great variation with pH. The form of the curve suggests a relationship to the com-

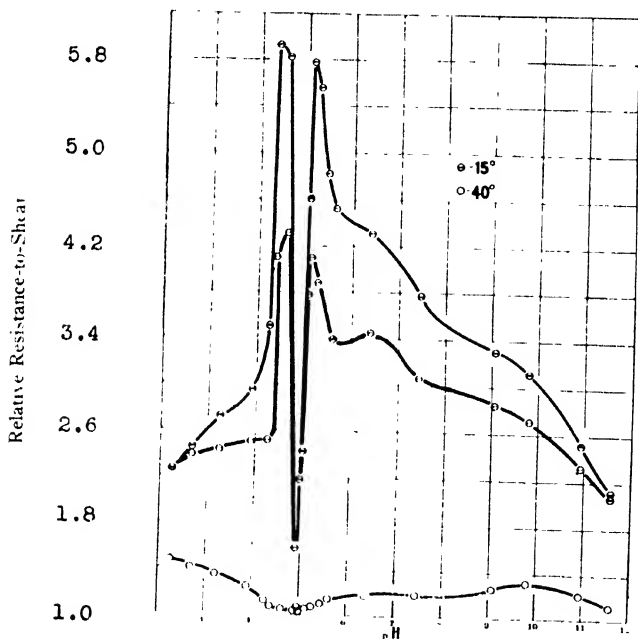


FIG. 10. Influence of pH and temperature upon the relative resistance-to-shear of 0.38 per cent gelatin systems. pH's adjusted with acetic acid and sodium hydroxide. Lower 15° curve after 24 hours, upper curve after 48 hours.

bination curve and those properties to which the equations of the Donnan membrane equilibrium have been applied. At 25°C . and lower, the curves take on an entirely different form. In the region of the two minima at higher temperatures, the temperature coefficient becomes relatively great and the minima are replaced by maxima except in a very narrow region near pH 4.95 where the sudden rise in tyndall effect takes place. At this point, the precipitation tendency is so pronounced as to cause either a turbidity preventing observa-

tions of optical activity or—if a thin layer is used—an actual minimum in specific rotation (cf. Figure 9). With decreasing temperature, the specific rotation and gel-forming tendency increase in the region between pH 5 and 8, partially masking the minor maximum near pH 8.

The parallelism between optical activity and gel formation is illustrated by Figure 10 in which the dependence of resistance-to-shear

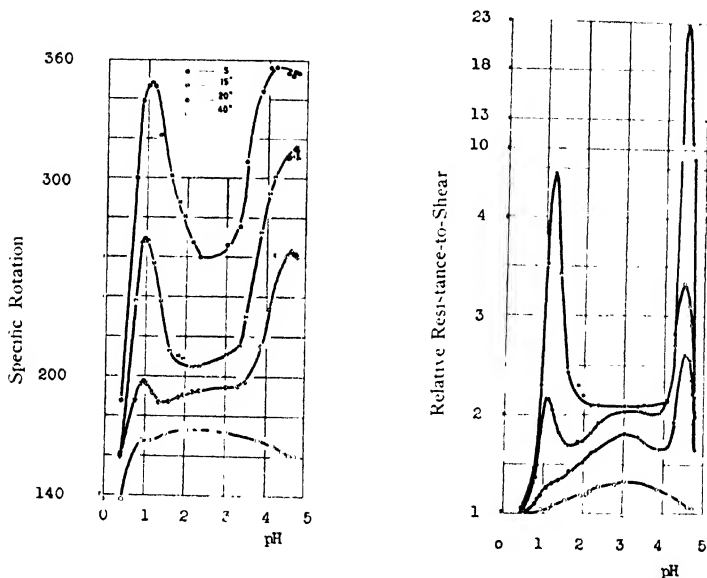


Fig. 11.—Influence of pH and temperature upon the specific rotation and relative resistance-to-shear (gel strength) of 0.38 per cent gelatin systems. pH's adjusted with HCl

upon pH and temperature is shown. The maximum gel strength appears on either side and very near to the optimum precipitation point or isoelectric point, illustrating the general rule that gel formation takes place under conditions which are just adjacent or boundary to those leading to readiest precipitation or coagulation. Over a narrow region at the isoelectric point at pH 4.95, the gel formation is small;" the sharpness of the minimum at this point resembles closely the maximum in tyndall effect at the same pH.

* Contrary to the usual assumption. See for instance Michaelis and Nakashima, *Biochem. Zeit.*, **143**, 484 (1923). The sudden change in conditions at this critical point appears to have been overlooked by Gerngross and Bach in the paper already mentioned

The range of pH attainable with acetic acid is of course more limited than with stronger acids. With hydrochloric acid, the influence of pH's as low as 0.5 can be observed as shown in Figures 11 and 12. For pH's above 2.5, the curves of specific rotation and resistance-to-flow with hydrochloric acid parallel those with acetic acid. However, below pH 2.5 and at low temperatures, a new and en-

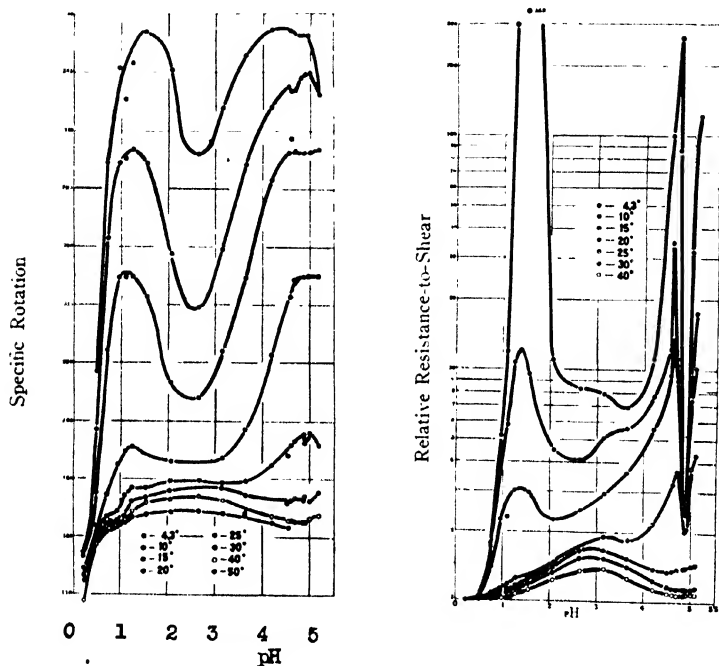


Fig. 12.—Influence of pH and temperature upon the specific rotation and gel strength (relative resistance to shear) of 0.62 per cent gelatin systems containing HCl.

tirely unexpected phenomenon appears in the form of another region of high specific rotation and great gel strength at pH 1-1.5. Even at the higher temperatures, there is a distinct suggestion of irregularity in the curves at the low pH. At intermediate temperatures, the gradual and continuous transition from the high temperature type curve to the low temperature type is evident. The appearance of this fourth region of gel formation completes a certain symmetry in the behavior of gelatin with respect to pH, the center of reference being

the point of maximum tyndall effect at pH 4.95 for this particular gelatin. On either side and immediately adjacent to this point are two regions of gel formation. Then on either side and at a distance of about 3-3.5 pH units appear two more regions of gel formation near pH 1-1.5 and near pH 8.5. Figure 13 shows that the gel forma-

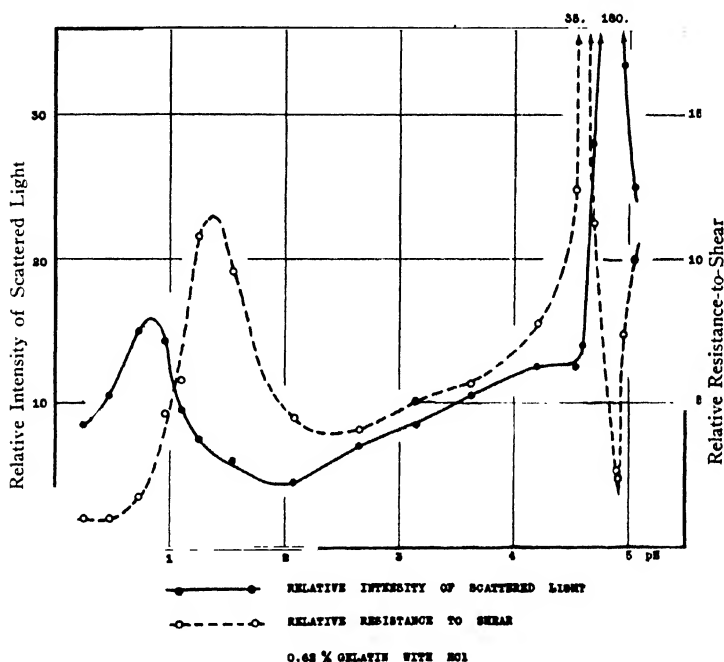


FIG. 13.—Relationship between precipitation tendency (as revealed by the tyndall effects) and gel strength. The tyndall effect curve is taken from recent unpublished work with Mr. G. H. Joseph.

tion at low pH is also associated with a maximum tyndall effect or a precipitation tendency, but no more congruent with it than are tyndall effect and gel formation at pH 4.95. Although hydrolysis of the gelatin is hastened by pH's as low as 0.5-1.0, the decrease in tyndall effect, specific rotation and gel formation below pH 1 is not due to hydrolysis; the hydrolysis, even at this pH is sufficiently slow to allow the reversibility of properties to be shown upon increasing the pH again.

Figures 14 to 17 show similar curves for hydrobromic, citric,

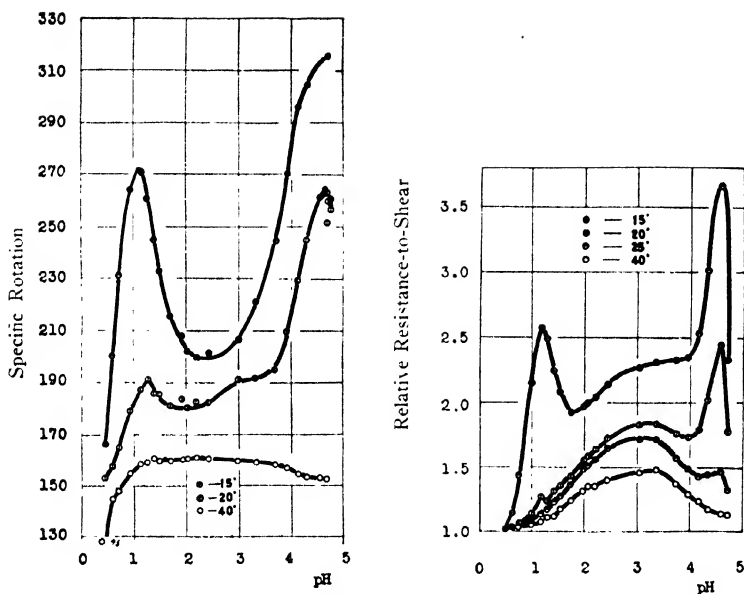


FIG. 14.—Influence of pH and temperature upon the specific rotation and gel strength (relative resistance to shear) of 0.38 per cent gelatin systems containing HBr.

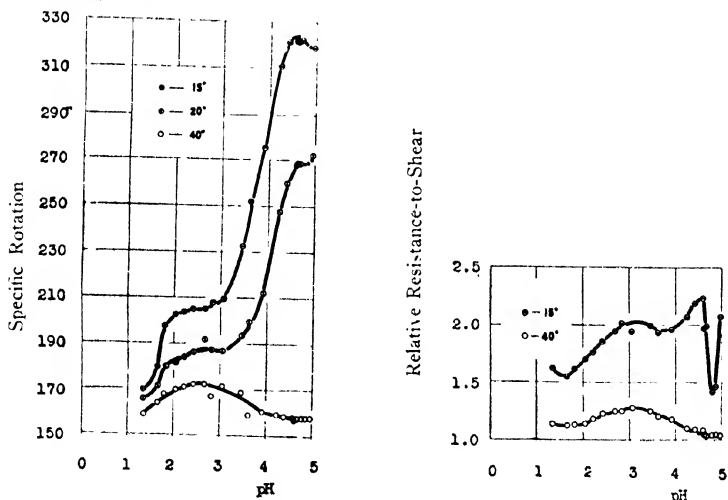


FIG. 15.—Influence of pH and temperature upon the specific rotation and relative resistance-to-shear (gel strength) of 0.36 per cent gelatin systems containing citric acid.

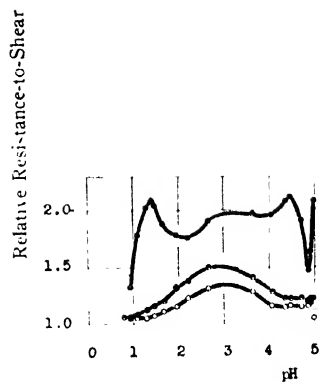
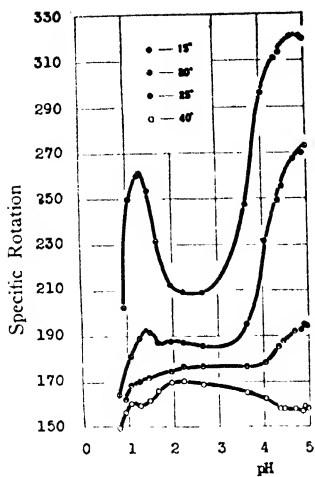


FIG. 16.—Influence of pH and temperature upon the specific rotation and gel strength (relative resistance-to-shear) of 0.30 per cent gelatin systems containing oxalic acid

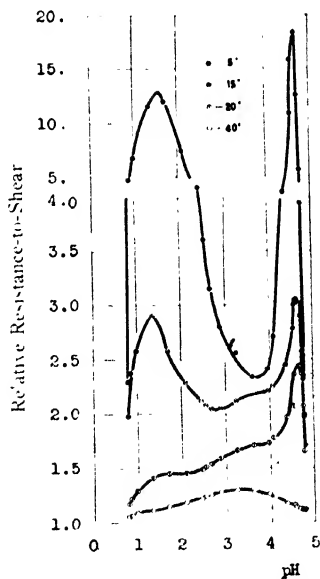
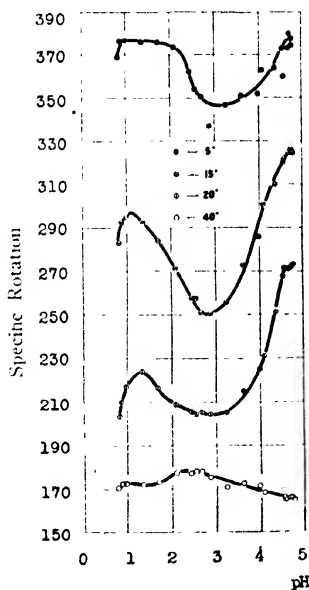


FIG. 17.—Influence of pH and temperature upon the specific rotation and gel strength (relative resistance-to-shear) of 0.38 per cent gelatin systems containing sulfuric acid.

oxalic, and sulfuric acids. The general relations remain the same, particularly with respect to the parallelism between specific rotation and resistance-to-shear. Hydrobromic, oxalic, and sulfuric acids all give the maximum gel strength and specific rotation at low pH. The breadth of the maximum is distinctly greater with sulfuric acid than with hydrochloric acid. In the case of citric acid, the maximum at low

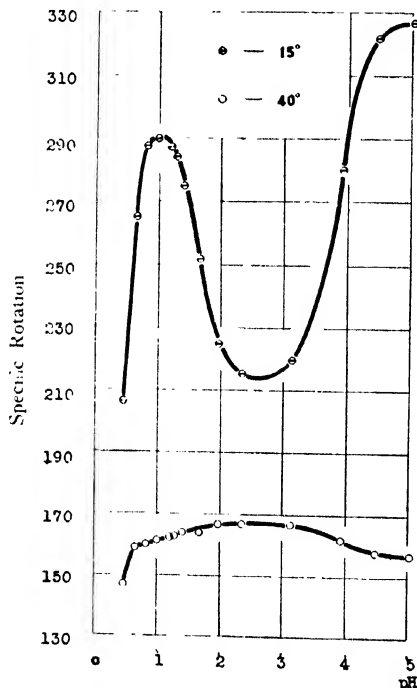


FIG. 18.—Influence of pH (HCl used) and temperature upon the specific rotation of the technical hide gelatin from which the de-ashed material was prepared. Concentration—0.375 per cent.

pH is lacking probably because of secondary effects arising from the excessive concentration of citric acid necessary to attain a low pH.

That this curious behavior at low pH is not due to modification of the gelatin during purification and de-ashing is shown by the curves of Figures 18 and 19 for two commercial gelatins containing the normal ash and impurities. These show a negligible influence upon the pH's at which maximum and minimum appear. The pigskin gelatin with isoelectric point at pH 8 also shows the maximum spe-

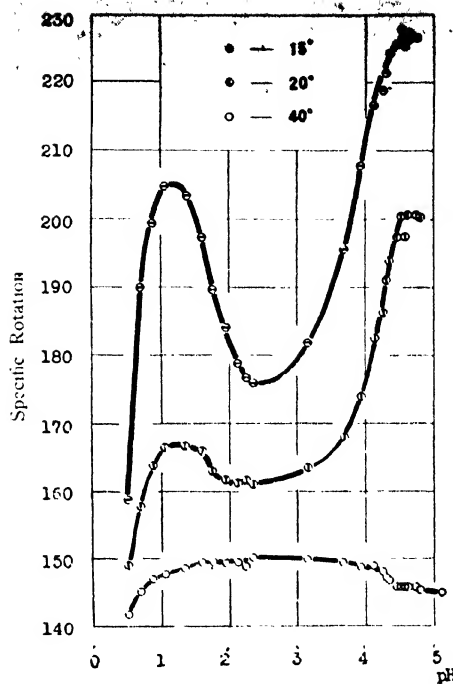


FIG. 19.—Influence of pH and temperature upon the specific rotation of 0.41 per cent Delft blended bone gelatin systems containing HCl.

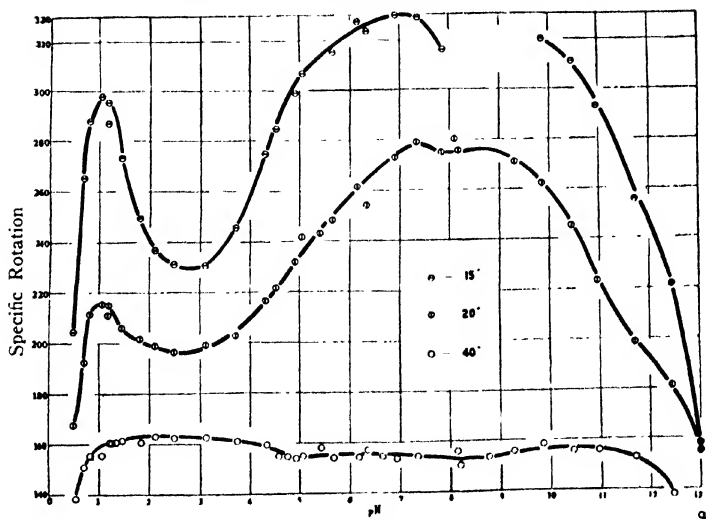


FIG. 20.—Influence of pH and temperature upon the specific rotation of 0.4 per cent pigskin gelatin systems containing HCl and NaOH.

cific rotation at low pH as may be seen in Figure 20. The usual behavior near pH 5 is suggested at 40° C. but is totally lacking at low temperatures. This gelatin remains anomalous with respect to specific rotation at pH 8.

The similarity of gel formation in gelatin systems with gel formation in disperse systems in general, particularly with respect to the influence of previous history, is illustrated by Figure 21. The strength of a gel formed at 15° C. is greater than one formed at 20° C. for

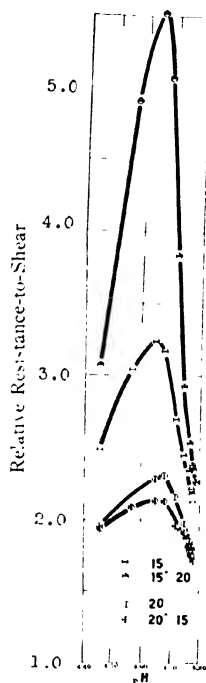


Fig. 21—Influence of thermal history upon the gel strengths of 0.38 per cent gelatin systems containing various quantities of hydrobromic acid. Total age in each case is 48 hours. Changes in temperature were made at the 24th hour. 15°-20° means 24 hours at 15° following 24 hours at 20° C.

the conditions represented by the figure, and yet, when the total history is split between one period of 15° after a period of 20°, the gel strength is actually much greater than in the gel kept continuously at 15° C. On the other hand, if the lower temperature period precede the higher temperature period (20°-15° C.), the gel strength is even less than that of the gel continuously at 20° C.

These facts and observations, it is believed, illustrate the claim made at the beginning that more information and data are required for understanding the colloid behavior of the proteins. Even a material like gelatin, as much studied as it has been already, may still be made with a simple technic to reveal a behavior entirely unexpected on the basis of current views and theories. A slavish attachment to such views and theories therefore prevents the discovery of important facts.

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MASS ACTION EFFECTS IN THE INTERACTION OF GELATIN AND ACIDS

BY W. K. LEWIS AND C. F. DANIEL

In treating the interaction of gelatin with acid, Procter¹ and later Procter and Wilson² claim that the phenomena follow the Ostwald hydrolysis equation for a monoacidic base,

$$f = y/(y + k),$$

where f is the fraction of the total base in the solution which has combined with hydrogen ion, y is the hydrogen ion concentration and k is the hydrolysis constant. Finding that the data did not accord with this equation for monoacidic base they concluded that the base must be diacidic, in which case the equation has the form,

$$f = y/(y + k_1) + y/(y + k_2),$$

k_1 and k_2 being the hydrolysis constants of the two basic groups. They do not discuss the justification of applying this equation to a material such as gelatin, but from a study of this part of their article it would seem justifiable to infer that they really consider gelatin as a diacidic base. Since they give its equivalent weight as 839, this would correspond to a molecular weight for gelatin of 1678. However, from the other work of these authors it seems unlikely that they would be willing to accept this particular conclusion.

If the mass action concept is to be applied to gelatin, it seems imperative that one start with the assumption that gelatin is a material of very high molecular weight. Since all the data indicate that its equivalent weight is relatively low, there must be a large number of basic groups per molecule of gelatin. The following treatment is based on this assumption:

NOMENCLATURE.

- α = mols gelatin per liter.
- w = number of amino-groups per mol of gelatin.
- y = hydrogen ion concentration.
- n = the number of the particular amino group in the gelatin molecule under discussion, starting with the strongest and numbering in order of strength.

¹ *J. Chem. Soc.*, 105, 818 (1914).

² *Ibid.*, 109, 807 (1916).

- z_1 = concentration of positive charges due to combination of strongest amino-group with hydrogen ion.
 z_2 = same for second strongest amino group, etc.
 z_w = same for weakest amino group.
 z = concentration of positive charges due to all amino groups combined.
 β = equivalents of gelatin per liter = α_w .
 K_1 = hydrolysis constant of strongest amino group.
 K_2 = hydrolysis constant of second amino group, etc.
 K_w = hydrolysis constant of weakest amino group.
 α = conc. of gelatin anion — (RCOO^-).
 γ = equivalent concentration of gelatin as an acid.
 k = average equilibrium constant for ionization of gelatin as an acid.
 $c = k\gamma$ = constant for one gelatin concentration.

Since the equivalent weight of gelatin is of the order of magnitude of 800 or greater, it is probable that the distances between adjacent available amino groups in the gelatin molecule are considerable. This makes it likely that the reactivity of any given amino-group with hydrogen ion is not appreciably affected by similar interaction of other amino groups in the molecule. If this be granted, one can immediately apply the Procter-Ostwald equation to each individual amino group, i.e.,

$$z_1 = \alpha\gamma/(\gamma + K_1); \quad z_2 = \alpha\gamma/(\gamma + K_2); \quad \text{etc.}^3$$

However,

$$z = z_1 + z_2 + \dots + z_w,$$

$$\text{whence, } z = \alpha\gamma \left(\frac{1}{\gamma + K_1} + \frac{1}{\gamma + K_2} + \dots + \frac{1}{\gamma + K_w} \right)$$

$$= \alpha\gamma \sum \frac{1}{\gamma + K} = \frac{\beta\gamma}{w} \sum \frac{1}{\gamma + K}. \quad (1)$$

Since under the summation sign (Equation 1) there are w terms, it will be obvious that the expression

$$\frac{1}{w} \sum \frac{1}{\gamma + K}$$

is an arithmetic mean, equal to $\frac{1}{\gamma + K_{av}}$.

If we let $x = n/w$, keeping in mind the fact that n is an integer with increments of unity, one can write,

$$\frac{1}{w} \sum \frac{1}{\gamma + K} = \sum \frac{\Delta n/w}{\gamma + K} = \sum \frac{\Delta x}{\gamma + K}.$$

³ The ordinary method of applying the mass action law to a polyacidic base is to assume that reaction of the second basic group is always preceded by that of the first, and so on. It is, however, easy to show that the method here employed is quantitatively equivalent, provided the proper relations exist between the ordinary constants of the basic groups and the ones here used. This method simplifies computation in this specific case.

For each value of n the corresponding value of K is definite though at present unknown. In other words, K is a fixed function of n and therefore also of x , i.e., $k = f(x)$. Since w , the number of amino groups per gelatin molecule, is large, the value of this sum will not differ materially from the expression

$$\int_0^1 \frac{dx}{y + K} = \int_0^1 \frac{dx}{y + f(x)}.$$

Hence, one can write,

$$z = \beta y \int_0^1 \frac{dx}{y + f(x)}. \quad (1a)$$

From equation (1) one can immediately draw certain interesting and important conclusions. In the first place, the single-term Procter equation can be correct only in case the hydrolysis constants for all amino groups of the gelatin molecule are numerically identical.⁴ The probability of this is too slight to justify serious consideration. The two-term Procter equation would demand the assumption that the amino groups are divided into two classes, equal in number, all groups of each class having the same hydrolysis constant. This seems equally improbable. It is difficult to justify the Procter equation on theoretical grounds.

In the second place, inspection of Equation (1), when written in the form,

$$z/y = \frac{\beta}{w} \sum \frac{1}{y + k},$$

makes it obvious that this equation demands that z/y decrease with the increasing values of y . Table I shows Loeb's data⁵ (y, z_0) for z and y for gelatin hydrochloride, arranged in the order of increasing values of y . It will be noted that, at low values of y , z/y increases greatly, goes through a sharp maximum and then decreases as the above equation demands. This discrepancy at low values of y demonstrates that gelatin does not follow the simple mass action expression. Indeed, it proves that isoelectric gelatin acts as a much weaker base than gelatin which has already partially reacted with acid.

The discrepancies at low values of y are not of a character to

⁴ The hydrolysis constants of the various amino groups can be equal only in case the constants as ordinarily expressed, assuming ionization of the first group to precede that of the second and so on, have the following values for successive amino groups.

First amino group,

K

Second amino group

$\left(\frac{2w}{w-1}\right) K$

Third amino group $\left(\frac{3w}{w-2}\right) K$, etc. Last amino group, $w^2 K$

⁵ Loeb, *J. Colloid Physiol.*, 3, 691 (1920-21); Loeb, "Proteins and Theory of Colloidal Behavior," 175 (1922).

be explained on the assumption that the hydrogen ion is adsorbed by the gelatin, because adsorption phenomena are characterized by the fact that, particularly at low concentrations of the material adsorbed (in this case the hydrogen ion), the ratio of amount adsorbed to concentration of the adsorbed material decreases rapidly as this concentration is increased.

As so clearly shown by Loeb, gelatin acts both as acid and as base and, as indicated by his data, its strength as an acid is much greater than as a base, though its equivalent weight as an acid is approximately three times its equivalent weight as a base. In strongly acid solutions one would expect the activity of the weak gelatin acid groups to be effectively suppressed, but, as one approaches the isoelectric point, they should come into action; in other words, there should be a certain amount of internal compensation. It is obvious that a mass action equation analogous to (1) should govern the ionization of the gelatin as an acid. Since this ionization on the acid side of the isoelectric point is only a small correction term, it will lead to no serious error to assume an average value, k , for the dissociation constants of the acidic groups of gelatin. Calling γ the equivalent concentration of the gelatin as an acid, and u the concentration of negative charges on the gelatin due to ionization of its acidic groups, the mass action law requires that $u = \frac{k}{y}(\gamma - u)$. Furthermore, on the acid side of the isoelectric point u will be small compared to γ and no serious error will arise from writing,

$$u = k\gamma/y.$$

As used by Loeb and Procter, z is the concentration of positive charges on the gelatin corresponding to external acid reacting with the gelatin, but the mass action expressions as represented by equations (1) and (1a) would give the total positive charges on the gelatin due to interaction with hydrogen ion from any source whatever. From these computed values one should therefore subtract any positive charges on the gelatin due to internal compensation, i.e., one should write,

$$z = \frac{\beta y}{\alpha} \sum \frac{1}{y + K} - \frac{k\gamma}{y} = \beta y \int_0^1 \frac{dx}{y + f(x)} - \frac{k\gamma}{y}. \quad (2)$$

The function $f(x)$ is unknown, but as a first approximation it will perhaps not be amiss to assume it linear in x , that is, to assume that the hydrolysis constant of successive amino groups differ by substantially equal increments. On this assumption, equation (1a) integrated, becomes

$$z = \frac{\beta y}{K_w - K_1} \ln \frac{y + K_w}{y + K_1} \quad (3)$$

and equation (2),

$$z = \frac{\beta y}{K_w - K_1} \ln \frac{y + K_w}{y + K_1} - \frac{c}{y}. \quad (3a)$$

Further, it can be shown that in the range of the data in question, these equations are good approximations, even though K as a function of x may differ quite widely from linear.

It is obvious that at high values of hydrogen ion concentration Equation 3 should be satisfactory. In this equation, β , the total equivalents of gelatin in the solution, is the asymptotic value of the acid combining capacity of the gelatin at high hydrogen ion concentration and can be determined with reasonable precision. A little study of the equation will show that the individual constants, K_1 and K_w , are not capable of exact evaluation unless the precision of determination of z as a function of y is very great. This is particularly true of K_1 . For Loeb's data on gelatin chloride (*loc. cit.*) at hydrogen ion concentrations above 46, we have estimated the values of k_1 and k_w as 1.4 and 95 respectively. Table I shows the values of z observed by Loeb [z_0] with the values calculated by Equation (3) [z_1].

In one sense Equation (3) is no more satisfactory than Procter's two-term equation, because both have three constants, the numerical values of which must be determined from experimental data. Granting sufficient constants in an equation, one can get an expression which will fit any curve. On the other hand, Procter's equation can be given a theoretical basis only by making difficultly justifiable assumptions, whereas equation (3) is theoretically sound and its only weakness lies in the fact that it assumes a certain type of change of K with x . However, some functional relation between K and x must exist, and, as indicated above, the data at present available are not sufficiently accurate to test other assumptions.

Granting these constants in Equation (3), the constant of the correction term in Equation (3a), $c (= ky)$, is readily computed from the values of z determined by Loeb for values of y below 50. For this we find 125. This gives as the final equation representing Loeb's data,

$$z = 15.7 y \log_{10} \frac{y + 95}{y + 1.4} - \frac{125}{y} \quad (4)$$

and in general, $z = 0.0245 \beta y \log_{10} \frac{y + 95}{y + 1.4} - \frac{.195\beta}{y}$. (4a)

The comparison of the values of z experimentally determined by Loeb [z_0] with those computed [z_2] from Equation (4) are found in Table I. Figure 1 shows the same data plotted as z/y vs. y . This form of plot is employed because it most emphatically brings out the discrepancies between computed and observed values of z at low hydrogen ion concentrations. If one plot z itself versus y one must either employ a scale which omits all high points or else one that crowds the low points too closely together. In Figure 1 the dotted curve represents values computed from the Equation (4) and the full curve the values computed from a single term Procter equation (see Table).

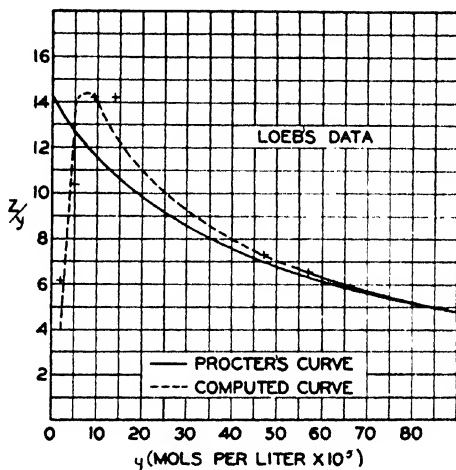


FIG. 1

the constants of which are chosen to make that curve fit the values of z determined by Loeb at high hydrogen ion concentration (i.e., above 50).

Procter does not report data on the amount of acid combined with gelatin at low hydrogen ion concentration. Indeed Procter undoubtedly did not know how to produce the isoelectric gelatin with which it would be necessary to start to make such data of any value. Consequently the correction term of Equation (3a) does not have to be used in interpreting his data. Furthermore, Procter worked at widely varying gelatin concentrations whereas Loeb kept his gelatin concentrations practically constant. Inspection of Equation (3) shows that the acid combined per equivalent of gelatin is a unique function

TABLE I

y	27	4.9	9.3	14.1	46.8	56.2	141	302	741	1023
z	16.5	51.4	132.5	200	343	372	477	608	609	600
$\frac{y+95}{y+1.4}$	24	15.8	9.8	7.04	2.94	2.62	1.66	1.31	1.13	1.09
$\log_{10} \frac{y+95}{y+1.4}$	1.38	1.20	0.99	0.85	0.47	0.42	0.22	0.12	0.052	0.038
z_1	61.7	92.3	145	189	346	372	488	570	607	614
$\frac{125}{y}$	46.3	25.3	13	9	3	2	1	—	—	—
z_2	15.4	67.0	132	180	343	370	487	570	607	614
z_3	16.5	51.4	132.5	200	343	372	477	608	609	600
$\frac{640}{y+45}$	13.4	12.8	11.8	10.8	7.0	6.3	3.4	1.84	0.82	0.60
$\frac{z_1}{y+45}$	6.1	10.5	14.3	14.2	7.3	6.6	3.4	2.0	0.82	0.59
$\frac{z_2}{y+45}$	5.7	13.7	14.2	12.8	7.3	6.6	3.5	1.9	0.82	0.60

N.B.—Explanatory Equations:

$$z_1 = 15.7 y \log_{10} \frac{y+95}{y+1.4} \quad z_2 = 15.7 y \log_{10} \frac{y+95}{y+1.4} - \frac{125}{y}$$

$$\frac{640}{y+45} = \frac{z}{y} - \text{Procter's type of equation for Loeb's data.}$$

of y . Hence, plotting z divided by gelatin concentration, i.e., z/β , versus y , one should get a smooth curve. Figure 2 shows Procter's data thus plotted and it will be seen immediately that the points are far more erratic than Loeb's data. The curve in Figure 2 represents Equation (3) as determined from Loeb's data, using however 780 as the equivalent weight of gelatin instead of 1560 as determined from Loeb's measurement. Procter's gelatin appears to have suffered progressive

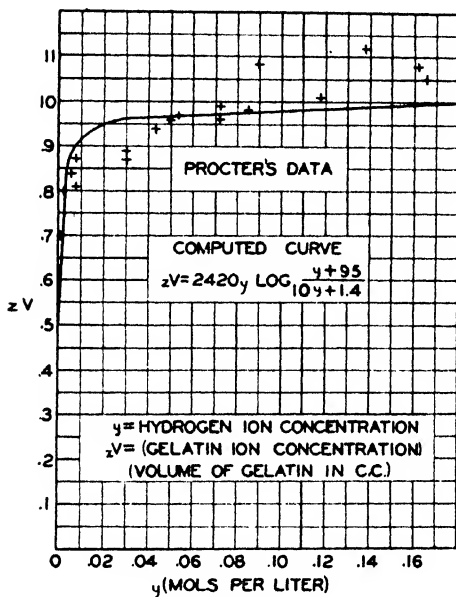


FIG. 2.

hydrolysis during the course of the experiments at high hydrogen ion concentration. It must be remembered that he operated in some cases at a concentration well above tenth normal in hydrogen ion. Nearly all of Procter's data were taken at gelatin concentrations greatly exceeding that used by Loeb. Since z is calculated by difference and since in the majority of Procter's measurements z is less than y , the precision of z is low. This fact, together with the probability of increased gelatin hydrolysis at the high hydrogen ion concentrations used, accounts for the erratic appearance of the points in Procter's plot. Despite this fact the maximum deviation of Procter's points

from the calculated value of z is less than 15 per cent and the average deviation only about 6 per cent.

The quantitative relationships here developed suggest certain qualitative conclusions of interest. Thus, while the data, which so clearly indicate internal compensation in the neighborhood of the isoelectric point, throw no light on the question as to whether the reaction of acidic and basic groups of the gelatin itself is intermolecular or intramolecular, it seems likely that the combination is between groups in different molecules. This would to a degree tie together molecules of gelatin at the isoelectric point, but this intermolecular bonding would decrease rapidly as one leaves the isoelectric condition. As soon as hydrogen ion concentration is built up to a value of roughly 25 in Loeb's units, this type of molecular association would cease to be an important factor. This gives an explanation of the mechanism of the polymerization of gelatin in the neighborhood of the isoelectric point. Such polymerization has often been assumed, though in the past apparently without adequate justification.

Since viscosity as a function of hydrogen ion continues to increase far beyond this point, there must be some other important contributing cause. Many explanations have been offered, of which perhaps the most widely accepted are (1) increased hydration of the gelatin as hydrogen ion increases and (2) increased degradation of the gelatin itself by hydrolysis. Both of these seem to be decidedly *ad hoc* explanations. Since with increasing hydrogen ion concentration there is a marked increase of combination of hydrogen ion with the amino groups of gelatin, it of necessity follows that the corresponding anions of the acid added will be held by electrostatic attraction in the neighborhood of the amino groups. From the point of view of mobility, this is equivalent to an increase in the size of each molecule of gelatin and, since the average distance between the charged amino ion and the corresponding anion can be considerable, it follows that the fractional increase in effective molecular size will be large. This should result in increased viscosity as long as there is an increase in amount of acid combined with the gelatin. However, in strongly acid solutions, further increase in combined acid is negligible, but the added solute, which is undoubtedly highly solvated in solution, begins to compete with the gelatin molecules for solvent and this dehydration of the gelatin results in a shrinkage, thus producing the maximum in the viscosity curve.

A similar point is the discrepancy between the action of sulfuric and other acids on gelatin so clearly brought out but not explained by Loeb. If the only effect is combination of amino groups with hydrogen ion, the extent of that combination should be independent of the source of the hydrogen ion. However, in the case of sulfuric,

for a given amount of acid combined with the gelatin, the corresponding hydrogen ion concentration is abnormally high. Sulfuric as a dibasic acid is characterized by the fact that both its hydrogen ions are very strong. Since the equivalent weight of gelatin as a base is 800 or more, it follows, if one assumes that the free amino groups are at all regularly distributed in the gelatin molecule, that the distance between adjacent amino groups is considerable. If, now, a hydrogen ion from sulfuric acid combines with an amino group, the anion cannot move a great distance away from this group. However, the second hydrogen ion of the sulfuric will dissociate to a large degree, but in turn will be held by electrostatic attraction in the neighborhood of the sulfate ion from which it came. Consequently this particular hydrogen ion, while adding to the hydrogen ion concentration of the solution as a whole, is not entirely free, at least not sufficiently so to migrate to and combine with another amino group. In consequence one would anticipate an abnormally high hydrogen ion concentration for a given amount of combination between sulfuric and the gelatin base. However, in the case of ordinary polybasic acids, in which the second hydrogen is weak compared to the first, the dissociation of this second hydrogen would be a minor factor and the acid would behave toward gelatin as a monobasic acid. It will be noted that this is exactly the situation disclosed by Loeb's data.^a

Summary.

Attention is called to the fact that Procter's mass action equation for the reaction of gelatin in acid implies either that the molecular weight of gelatin is not greater than double its equivalent weight, or else that all the amino groups in gelatin have the same acid strength. It is also shown that this equation breaks down completely in the face of Loeb's data obtained at low hydrogen ion concentrations. It is demonstrated that isoelectric gelatin acts as a weaker base than gelatin which has already combined with some acid. It is further pointed out that this behavior can be quantitatively explained on the assumption of internal interaction of amino groups and carboxyl groups in the gelatin itself. A general mass action expression for the interaction of gelatin and acid is derived, including a correction term for internal compensation of the basic and acidic groups of gelatin in the neighborhood of the isoelectric point. Qualitative implications of this internal compensation's effect on the viscosity of gelatin solutions are discussed.

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^aLoeb, "Proteins and the Theory of Colloidal Behavior," p 175, Tables XXXII and XXXIII.

HELMHOLTZ DOUBLE LAYER RELATED TO IONS AND CHARGED PARTICLES

By E. F. BURTON

1. Electro-endosmose and Related Phenomena:

The so-called Helmholtz double layer connotes a mechanical explanation of the phenomena included under the general title of electro-endosmose. The term electro-endosmose is applied to the phenomenon of the transfer of liquids through capillary tubes under the action of an electric field set up throughout the tubes by electrodes placed at the ends of the tubes and maintained at a given difference of potential. The experiments on single capillary tubes have been extended to porous diaphragms which are treated merely as collections of fine capillaries. The laws governing this action have been very fully worked out by a succession of scientists.

Although this phenomenon of electro-endosmose has been given particular attention, it is merely one of four phenomena which treat of the electrical forces set up by the relative motion of solids and liquids, or, of such relative motions set up by applied electromotive forces. The correlation of these phenomena may be seen in Table I.

TABLE I

<i>A</i>	<i>B</i>
Motion caused by applied E.M.F.	E.M.F. set up by impressed motion
I. Liquid moving through stationary solid tubes. Electroendosmose. ¹	I. Liquid forced through stationary solid tubes. Helmholtz-Billiter. ²
II. Solid particles moving through stationary liquids. Cataphoresis. ³	II. Solid particles dropped through stationary columns of liquid. Dorn effect. ⁴

It is at once apparent that there is an intimate relation existing between these phenomena, *B* being in general the converse of *A*, and,

¹ Wiedemann, *Elektricität*, 1, 1007 (1893). Quincke, *Pogg. Ann.*, 113, 513 (1861). Helmholtz, *Ann. d. Phys.*, 8, 337 (1879); *Memoirs Lon. Phys. Soc.*, 1888. Lamb, *Brit. Assn. Rep.*, 495 (1887). Perrin, *Jour. chim. phys.*, 2, 607 (1904); 3, 50 (1905). Elssasoff, *Z. phys. Chem.*, 79, 385 (1912). Briggs, Bennett, and Pierson, *J. phys. Chem.*, 22, 266 (1918).

² Burton, "Physical Prop. of Coll. Sol." (Longmans, Green, 1921, p. 132). M. E. Laing, *J. phys. Chem.*, 28, 673 (1924). Mukherjee, *Proc. Roy. Soc.*, 103, 102 (1923).

³ Freundlich, "Kapillarchemie." 3rd ed., p. 335. Helmholtz, *loc cit.* (1). Billiter, *Z. phys. Chem.*, 48, 542 (1904).

⁴ Freundlich, "Kapillarchemie" (*loc cit.*). Dorn, *Ann. d. Phys.*, 5, 20 (1878); 9, 513 (1880); 10, 46 (1880). Billiter, *Ann. d. Phys.*, 11, 927 (1903). Freundlich and Mäkelä, *Z. Elektrochem.*, 25, 161 (1909); Burton and Currie, *Phil. Mag.*, 40, 194 (1925).

within both *A* and *B*, (II) is the converse of (I). The common feature of all is illustrated by the explanation which has been offered by the so-called Helmholtz double layer.

Historically the discussion of electroendosmose and cataphoresis came first (Wiedemann). In order to explain these curious motions, Quincke suggested that the solid in contact with the liquid became charged in some way with electricity of one sign, while in the immediate vicinity of the solid wall there was a layer of electrical charges of the opposite kind, exactly equal in magnitude to the first. Helmholtz first offered a mathematical treatment of Quincke's suggestion and

HELMHOLTZ DOUBLE LAYER

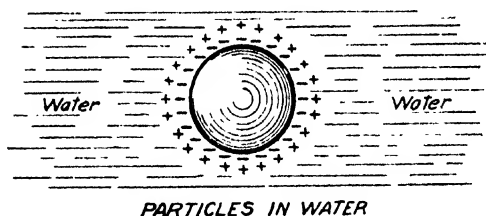
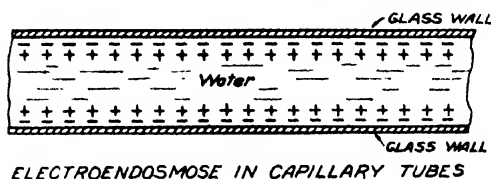


FIG. 1.

arrived at certain formulæ the truth of which could be—and in fact, was—tested and proved to be true (Fig. 1). The picture presented is consequently known as the Helmholtz double layer, which was further dealt with several years ago by Lamb.

When two electrodes, positive and negative, maintain a difference of potential at the ends of the capillary tube, the liquid is dragged through towards the negative electrode and slips as a sleeve through the tube. A similar explanation was offered of the movement of solid particles through stationary liquid media.

The assumption adopted by both Helmholtz and Lamb, in which they have been followed by others, is that the total thickness of the double layer is just of molecular dimensions, e.g., it is assumed that the

charged particle plus the contiguous liquid layer gives an entity which is electrically neutral. This assumption of the thickness of the layer is not implied in the Helmholtz test formula for electroendosmose, which is as follows:⁵

$$v = \frac{r^2 V E D}{4 L \eta}$$

where

v = volume of liquid transported per sec. through a tube of radius r and length L ;

η = coefficient of viscosity of the liquid;

D = dielectric constant of liquid;

V = difference of potential between stationary charged layer and the outer Helmholtz layer;

E = the electromotive force applied to electrodes at the ends of the capillary tube.

Consequently, the fact that this formula has been found to hold true for various experimental tests does not demand one's assent to the assumed thickness of the outer layer.

By considering the motion of a small cylinder of liquid taken parallel to the axis of the capillary tube and replacing this cylinder by a small solid cylinder stationary relatively to the liquid, one deduces that if the liquid as a whole is at rest and the solid cylinder in motion, it will have a velocity as given by the equation:

$$u = \frac{V E D}{4 \pi L \eta}.$$

In order to explain this phenomenon of cataphoresis, Helmholtz,⁶ after postulating the double layer, says, "On the whole, the algebraic sum of the two charges on the two layers equals zero, and the center of gravity of the complete system, solid particle (e.g., negatively charged) and surrounding (positively) charged fluid layer taken together, cannot be moved by the electric forces which arise from the potential fall in the liquid through which the current passes. However, the electric force will tend to bring about a displacement, relatively to each other, of the positively charged fluid layer and the negatively charged particle, whereby the fluid layer follows the flow of positive electricity while the positive moves in the opposite direction. If the liquid were a perfect insulator the new position would still be a condition of equilibrium. Since, however, through the displacement of the layers, the equilibrium of the galvanic tension between the solid particle and the liquid is dis-

⁵ Freundlich, "Kapillarchemie," 3rd ed., p. 329.

⁶ *Loc. cit.* (1).

turbed, and, on account of the conductivity of the liquid, always seeks to restore itself, the original state of electrical distribution will tend to be continually reproduced and so new displacements of the particle with respect to the surrounding liquid will continually occur."

As the conception held of the Helmholtz double layer was that just outside a charged surface (or charged particle) and within *molecular distance* of this surface there existed a layer of oppositely charged ions making up a total charge equal and opposite to that on the surface itself, it was thought that there could not be any mutual action between two such particles. (See Svedberg,⁷ Perrin,⁸ Porter and Hedges⁹). It is on this account that the recent work of Milner,¹⁰ Ghosh,¹¹ and Debye¹² on the complete dissociation of strong electrolytes, has an important bearing on the theory of the stability of colloidal solutions.

2. Mutual Actions of Ions in Electrolytes:

As usually presented, the theory of the partial dissociation of strong electrolytes defines the conductivity in terms of the concentration and the mobilities by such a relation as

$$k \propto m(u + v)$$

where k is the conductivity of the solution, m is the concentration in gram-molecules per unit volume and u , v are the mobilities of the ions. As the solutions become more concentrated the conductivity per mol. (the molecular conductivity) decreases and this is explained by assuming that only a portion of the m gram-molecules are dissociated into ions—a portion which decreases as the concentration increases. So we have the relation:

$$k \propto \alpha m(u + v)$$

where α is a fraction, the so-called degree of dissociation.

An equally reasonable assumption would be that m remained constant while u and v decreased constantly with increasing concentration and so lessened the molecular conductivity. This is the view recently worked out by Debye, based on extensive work of some of the leading American chemists.

From another point of view, the use of the osmotic pressure equation in its ordinary form:

$$PV = nRT$$

⁷ Svedberg, *Colloid Chemistry* (Chem. Cat. Co., 1924), p. 102.

⁸ Perrin, *Ann. Chim. Phys.* (8), 18, 5, (1909); *Atoms* (tr. Hammick, Constable, 1916).

⁹ Porter and Hedges, *Phil. Mag.* (6) 44, 641, (1922).

¹⁰ Milner, *Phil. Mag.* 23, 551 (1912); 25, 743 (1913); *Trans. Far. Soc.*, 15, 148 (1919).

¹¹ Ghosh, *J. Chem. Soc.*, 113, 449, 627, 707, 790 (1918).

¹² Debye and Hückel, *Phys. Zeit.*, 24, 185 (1923).

also takes for granted that there are no mutual forces between the ions of an electrolytic solution. The correction of this view brings in the virial due to Clausius.¹³ The virial is an analytical expression for the total energy of molecules of gas in a volume in terms of the instantaneous values of the coordinates of the molecules and the values of the components of the forces acting upon them; this expression includes the ordinary pressure term ($3/2 RT$) and, also, the energy due to the mutual action of the molecules. This latter term may be shown to be given by the expression

$$\frac{1}{2} \sum v \varphi(v),$$

when $\varphi(v)$ is the force between two molecules distant v apart. Consequently the equation for one gm. molecular weight becomes

$$\sum \frac{1}{2} m V^2 = \frac{3}{2} RT + \frac{1}{2} \sum v \varphi(v),$$

where m , V , R and T have their ordinary significance and the summation $\sum v \varphi(v)$ is made for every pair of molecules. This equation is taken over for the treatment of osmotic pressure of solutions and, if there is a mutual action between the ions of the solution due to their electrical charges, there will be a potential energy term, $\frac{1}{2} \sum v \varphi(v)$, to be calculated. This is the problem attacked by Milner and Debye from different points of view.

Milner solved the problem in a direct way—a treatment which is recognized as an outstanding accomplishment which showed that many of the difficulties of the theory of partial dissociation could be met by assuming mutual action on the part of both positively and negatively charged ions. Ghosh attempted also to account for the anomalies of strong electrolytes by assuming complete dissociation together with electrostatic forces between the ions.

Debye has developed a method of calculating the energy furnished by the above term $\frac{1}{2} \sum v \varphi v$ in a new and indirect method. Expressing the thermodynamic potential, G , by the equation $G = S - \frac{U}{T}$, he divides the energy U into two parts, i.e., $U = U_k + U_e$, U_k being that given by the classical theory and U_e being an added term due to the mutual action of the ions on account of their electrical charge. He then sets out to find U_e . In order to accomplish this, Debye calculates the electrical potential at a point in a liquid medium containing ions both positive and negative, and then takes as the potential energy the ordinary expression: one half the product of the charge and the potential.

At a point, P , in the medium surrounding a particular ion, say positive, let the potential have a mean value ψ ; if another positive ion is brought up to this point the work done is $+\epsilon\psi$ where ϵ is the charge

¹³ See Jeans, "Dynamic Theory of Gases," p. 143.

on an ion; if a negative ion is brought up then the work gained will be $-\epsilon\psi$. In an element of volume, dV at P , one would have according to the Maxwell-Boltzmann¹⁴ principle:

$$nc \frac{-\epsilon\psi}{kT} dV \text{ positive ions and } nc \frac{+\epsilon\psi}{kT} dV \text{ negative ions,}$$

(where n = the number of molecules per cc. supposed to be univalent and completely dissociated, and k is the Boltzmann constant, which equals $\frac{R}{N}$, R being the universal gas constant and N Avogadro's number). From these two expressions the density, ρ , at the point P is determined, viz.:

$$\rho = -\frac{2n\epsilon^2}{kT} \cdot \psi, \text{ approximately,}$$

and, by the use of Poisson's equation

$$\nabla^2\psi + \frac{4\pi\rho}{D} = 0$$

the relation

$$\nabla^2\psi = K^2\psi$$

falls out, where $K^2 = \frac{8\pi n\epsilon^2}{DkT}$, in which D is the dielectric constant of the medium. This differential equation is solved, constants of integration determined and a value of potential energy of all the ions deduced. This work of Debye has been generally accepted as marking a great step forward in explaining the anomalies of strong electrolytic solutions.

In view of the application of this theory to be made later, it is desirable to give the general expression for K^2 in the case of a complex solution. Suppose there are S kinds of ions; let the numbers of ions per cc. be $n_1, n_2, \dots, n_i, \dots, n_s$ and the valencies be $Z_1, Z_2, \dots, Z_i, \dots, Z_s$. Then K^2 is given by

$$K^2 = \frac{4\pi\epsilon^2}{DkT} \cdot \sum n_i Z_i^2.$$

The physical interpretation of K is the following: calculation shows that $\frac{1}{K}$ has the dimensions of a length and the development of Debye's theory indicated that this length is a characteristic constant of the solution. If a plate is dipped in the solution, and takes up a definite

¹⁴Another example of this sort of treatment: Langmuir, *Phys. Rev.* 2, 450 (1918); 21, 419 (1923).

potential relatively to the liquid, the ions of the outer Helmholtz layer will be distributed according to the above equation and $1/K$ is the distance from the plate in which the electrical density of the ionic layer falls to $1/e$ of its value at the plate. $1/K$ is a quantity which measures the thickness of the Helmholtz outer layer.

Some years before Debye's work was published, Gouy¹⁵ had worked on a similar idea of the distribution of ions in a solution of an electrolyte, assuming complete dissociation. Gouy dealt with the law of distribution of positive and negative ions in a solution near a plate which, placed in the solution, assumes a given charge, and a definite potential relatively to the liquid.

He also finds that the outer Helmholtz layer has an electrical density which falls off according to an exponential law; the distance of the center of gravity of this ionic atmosphere, a , is given by:

$$a = \sqrt{\frac{DRT}{4\pi N^2 \epsilon^2 (n_a + n_c) N_c n_c \text{ (or } N_a n_a)}}$$

where D , R , T , N , ϵ are as before, n_a , n_c are the valencies of the anion and cation, and N_a , N_c are the number of gram ions per cc. in solution.

This may be compared with Debye's $\frac{1}{K}$ given by:

$$\frac{1}{K} = \sqrt{\frac{DRT}{4\pi N \epsilon^2 \sum n_i Z_i^2}}$$

In the development of these two theories the values of a and $\frac{1}{K}$ practically connote the same thing, only a slight difference being noticed in the way in which the valencies of the anions and cations are introduced. In Table II are given the values of a and $\frac{1}{K}$ for various types of strong electrolytes, using concentration of 0.001 gram molecular weights per litre.

TABLE II

$D = 80$	$K = 8.3 \times 10^7$	$T = 300$	$N = 6 \times 10^{23}$	$\epsilon = 4.77 \times 10^{-10}$
Type: Valency		Gouy's $a \times 10^7$	Debye's $\frac{1}{K} \times 10^7$	
uni-uni		9.1	9.1	
uni-di	}	5.29	5.74	
di-uni				
uni-tri	}	3.7	4.05	
tri-uni				
di-tri	}	2.3	3.6	
tri-di				
di-di		4.58	4.58	
tri-tri		3.0	3.0	

¹⁵ Gouy, *Journ. de phys.* (4), 9, 457 (1910).

These formulæ and results bring out two important properties of the Helmholtz double layer, viz.

- I. *The thickness of the outer Helmholtz double layer decreases as the concentration of the electrolyte increases; or addition of electrolytes to such a medium would depress the outer Helmholtz layer in towards the inner layer.*
- II. *For additions of electrolytes of the same molecular strength, the decrease in the thickness of the outer Helmholtz layer is greater the greater the valency of the ions, i.e., ions of high valency have a greater depressing effect than those of lower valency.*

Gouy brings out an additional point regarding the influence of the valencies of the ions, which is most significant for our problem.

- III. If at a point in an electrolytic solution near a charged plate U_c, U_c', U_c'' - - - etc., be the concentration of cations of valencies $n_c, n_c', n_c'',$ - - -, and U_a, U_a', U_a'' - - - be the concentrations at the same point of anions of valencies n_a, n_a', n_a'' - - -

$$\begin{aligned} \text{Then } U_c \frac{1}{n_c} &= U_c' \frac{1}{n_c'} = U_c'' \frac{1}{n_c''} = \dots \\ &= U_a \frac{1}{n_a} = U_a' \frac{1}{n_a'} = U_a'' \frac{1}{n_a''} - \dots \text{ etc.} \end{aligned}$$

From which Gouy concludes that if the cations have the same valencies, their concentrations remain throughout proportional to one another, and so for the anions; if the ions differ in valency, they are more concentrated or rarefied in the neighborhood of the surface depending on the valency.

For example, with ions of Sodium, Barium and Aluminium of concentrations $C_{Na}, C_{Ba}, C_{Al}, C_{Ba} = C_{Na}^2$ and $C_{Al} = C_{Na}^3$.

3. Ionic Atmospheres about Colloidal Particles:

We may say that all are agreed that the existence of the colloidal particle is fundamentally due to an equilibrium maintained between the forces of surface tension and the repulsion due to electrical charges. In their stable state, the existence of a very active Brownian movement does not seem to lead to collisions between particles which bring about an increase in size of the particles. As long as the particles remain small enough the disturbance due to the Brownian movement is sufficient to masquerade the small settling effect due to gravitation. Whether one denies the existence of mutual repulsion on the part of

colloidal particles or not, it is an undisputed fact that the particles of a stable colloidal solution do remain apart, although they are executing Brownian movements and so, one would judge, are being driven continuously into collision. A denial of the existence of mutual repulsion of such particles if they approach one another near enough, led Smoluchowski¹⁰ in his paper on a "Mathematical Theory of Coagulation" to assume that on near approach particles show mutual attraction. He made the following assumption: "The simplest assumption would be perhaps that the particles, on near enough approach to one another, are drawn together by capillary action; that union does not take place under normal conditions might be explained by a protective action of the electrical double layer, which one can picture to one's self as a sort of shell. On adding electrolytes, on account of the Freundlich absorption, a partial or complete discharge of the double layer takes place, which destroys its protective action, so that collisions and coalescence ensue. . . . We shall assume that each particle is surrounded by a protective sphere, so that neighboring particles execute their proper Brownian movements independently and undisturbed, so long as each one keeps without the protective spheres of its neighbors. But two particles are indissolubly united as soon as one of them pierces the boundaries of the protective region of a neighboring particle."

The more logical view of the distribution of ions in the Helmholtz double layer gives a far simpler and more acceptable explanation of the facts. The view of this distribution worked out by Gouy and Debye enables us to look upon single colloidal particles as bearing on their surfaces an effective charge which cannot be regarded as being neutralized by the outer Helmholtz layer until a surface is reached at such a distance from the boundary of the particle that the distribution of positive and negative ions becomes equal to the concentration in the medium itself. As a consequence, although at comparatively great distances from the particles (say, of the order $1.0 \mu = 10^{-4}$ cm.) the electrical force due to the particle is zero, and, consequently, two particles separated by such distances have no mutual repulsion, whenever two particles *do approach one another more nearly* they will mutually repel with a force which increases rapidly as the distance apart decreases. This explains why "union does not take place under normal conditions." There remains the question, "Why does the addition of electrolytes allow particles to come together?" In connection with the effect of added electrolytes on the disposition of ions in the outer Helmholtz layer, we may conclude from the propositions I, II, III above (1) that, as the concentration of the ions of given valency is increased, the distance of the center of gravity of the outer layer decreases, (2) that, for given concentration, ions of uni-, di-, tri-,

¹⁰ Smoluchowski, *Zeit. phys. Chem.*, **92**, 129 (1917).

etc., valency will give progressively thinner outer layers, the effect of the valency increasing exponentially with increasing valencies, and (3) that for liquids very slightly ionized the outer layer occupies a considerable thickness, many microns for pure water and still more for other liquids.

In view of these results we may construct a complete picture of the mechanism by which added electrolytes bring about coalescence, and, also, gain an insight into the abnormal effect of ions of different valencies. Let us replace Smoluchowski's assumptions given above by the following: (1) Particles on near enough approach to one another are held together by capillary action; (2) that union does not take place under normal conditions is accounted for by the mutual repulsion of the particles due to an effective charge, which becomes active when the particles approach one another within the limits of the diffuse Helmholtz outer layer; (3) added electrolytes, by suppressing the diffuseness of this outer layer, reduce the effective distance at which the repulsive force comes into play; and, finally, (4) by a discharge of the particle, the electrolytes destroy the source of the force which kept the particles apart.

The continuous Brownian movement will tend constantly to cause the particles to collide with one another. While the electrical charge is large enough, mutual repulsion will prevent the particles from approaching one another nearer than a certain distance. If, by the addition of electrolytes, the particles are discharged, which is an experimental fact, then that mutual repulsion which has prevented collisions is wiped out.

Proposition III of the previous section throws light on one of the most puzzling characteristics of electrolytic coagulation, viz., the peculiar valency relations expressed by the Hardy-Schulze law, that the coagulative power of uni-, di-, and tri-valent ions are in the ratios of $1 : x : x^2$ where x has a value, say, from 20 to 30. We find that if the concentrations, *near a charged surface*, of ions of valencies 1, 2, 3, in solutions of the same molecular strength in the bulk of the solution are denoted by C_1, C_2, C_3 , then

$$C_1 : C_2 : C_3 = C_1 : C_1^2 : C_1^3 :$$

$$\text{or} = 1 : C_1 : C_1^2.$$

From this we would gather that the resulting depression of the outer Helmholtz layer due to the addition of a *coagulating* trivalent ion would be much greater than for a similar divalent ion which in turn has a much greater effect than the univalent ion. The charge on the particle and that in the outer Helmholtz layer remaining the same, the resultant electrical forces between the two layers will be very much increased

by a nearer approach, and a time will come when the whole layout breaks down and the particle becomes partially or completely discharged. This discharging action would be much greater for trivalent than for divalent ions, much greater for divalent than univalent ions. We have also a reasonable explanation for the puzzling fact that the valency of the non-coagulating ion in the solution does not count in the action. From Gouy's result:

$$U_o^{\frac{1}{n_o}} = U_a^{\frac{-1}{n_a}}$$

and consequently a high concentration of cations (or anions) at a point in the solution means a very low concentration of the anions (or cations) at the point.

The interposition of these strong electrical forces between Helmholtz layers sufficiently close to one another, may bring about the adsorption of the ion of opposite charge in accord with the laws developed by Freundlich.

4. The Ionic Atmosphere and Electroendosmose:

The ordinary method of developing the formula giving the relation between the volume of water transported per second through a capillary tube, the applied electric field and other physical quantities involved, is to balance the frictional force due to viscosity against the electric force due to the external field acting upon the Helmholtz layer in the liquid bathing the wall; as Lamb expressed it "the electrical forces act on the superficial film of the liquid and drag the fluid, as it were, by the skin through the tube." This idea is quite at variance with our present conception of what is taking place at the wall.

The Helmholtz formula for electro-endosmose is usually deduced as follows:¹⁷

Let v = volume of liquid passing per second through a capillary tube of radius r .

Then u the average velocity of the liquid will be given by

$$\pi r^2 u = v \quad \text{or} \quad u = \frac{v}{\pi r^2}$$

If the layer actually in contact with the wall is at rest, i.e., if there is no slipping at the wall, the velocity gradient in the liquid, $\frac{du}{dr}$, may be

taken as constant and is usually written equal to $\frac{u}{\delta_v}$ where we indicate

¹⁷ For example, see Freundlich, "Kapillarchemie," or Creighton and Fink, *Electrochemistry* (John Wiley & Sons, 1924), p. 152.

by δ_v the perpendicular distance one must proceed from the wall in order to come to the place where the liquid has attained the velocity, u . The frictional force per unit area between the liquid at the wall and the flowing liquid will then be given by the ordinary viscosity formula:

$$F_v = \eta \frac{v}{\pi r^2} \cdot \frac{1}{\delta_v}$$

This frictional force, for steady slow motion, becomes equal to the electrical force due to the externally applied electromotive force acting on the Helmholtz layer. This electrical force per unit area will be

$$F_{el} = Hc$$

where H is the external electrical field given by the electromotive force applied at the ends of the capillary tube divided by the length of the tube and c is the charge per sq. cm. on the wall of the tube and consequently in the movable Helmholtz layer—

$$\therefore Hc = \eta \frac{v}{\pi r^2} \cdot \frac{1}{\delta_v}$$

Looking upon the double layer as an electrical condenser in a medium of dielectric constant, D , with difference of potential between the plates V we have:

$$V = \frac{c}{D \frac{1}{4\pi\delta_e}} = \frac{4\pi c}{D} \cdot \delta_e$$

where δ_e is the distance between the two Helmholtz layers. Substituting for c in terms of V we have the ordinary Helmholtz formula:

$$v = \frac{\pi r^2 \delta_v}{\eta} \cdot \frac{DVH}{4\pi\delta_e} = \frac{r^2 DVH}{4\eta} \cdot \frac{\delta_v}{\delta_e} \text{ or } V = \frac{4\eta v}{r^2 DH} \cdot \frac{\delta_e}{\delta_v}$$

Ordinarily δ_e and δ_v are taken both small and are put equal to one another, without any particular justification. V is then calculated in volts and results tabulated in that way.

We have seen above that δ_v is the distance from the wall where the liquid reaches its mean velocity. Extensive experiments on this phenomenon by Morrow¹⁸ shows that this distance is of the order of 0.5 cm. and consequently for capillary tubes the velocity continually changes, reaching a maximum along the central axis of the tube. Assigning a small value to δ_v comparable with δ_e can then have no meaning. According to the theory of the Helmholtz layer outlined above, the value of δ_e will depend upon the electrolytic content of the liquid

¹⁸ Morrow, *Proc. Roy. Soc. Lon.*, A. 76, 1905, p. 205.

in contact with the walls. Such facts call for a reconsideration of just what electro-endosmose is and why the liquid moves through to the capillary tubes when an external field is applied.¹⁹

Summary.

The quite recent work of Milner, Ghosh, Gouy and Debye on the complete dissociation of strong electrolytes has established beyond a doubt, almost, the fact of the mutual action of ions in solution. This consequently points to a mutual action of charged particles and also to the interaction of such colloidal particles and ions in solution.

That this mutual action of charged particles has not been properly realized is shown by the arguments used by Smoluchowski, Perrin, Porter and others; these writers have shown a tendency to be confined by the old idea of the Helmholtz double layer, viz., that immediately surrounding a charged wall or particle in contact with a liquid there is a layer of oppositely-charged ions, the thickness of this layer being of *molecular* dimensions.

The foregoing paper refers to the work of Milner who developed a method of calculating directly the interaction of ions and to the method Gouy and Debye employed in calculating the thickness of the outer Helmholtz layer, and its relation to the molality of the solution and the valency of the ions in solution. As a consequence one may form a reasonable picture of the charged colloidal particles with its surface charge and surrounding atmosphere of liquid containing positive and negative ions.

As a result of this picture of the distribution of charges relatively to the charged particle, explanations may be given as to the cause of the stability of colloidal particles, of the so-called Hardy-Schulze law of the coagulating power of electrolytes on dispersoids, and the motion of particles in an electric field, which is related to electro-endosmose.

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Toronto, Canada.

¹⁹ McBain, *J. Phys. Chem.*, **28**, 706 (1924).

X-RAYS AND COLLOIDS

BY GEORGE L. CLARK

I. Introduction:

The great contributions of X-ray science to the knowledge of the crystalline state of matter constitute some of the most brilliant pages in the record of scientific achievements of the past decade. The X-ray and the crystal spectrometer have added themselves to the list of the chemist's most valuable and powerful tools, just as they are to the physicist in sub-atomic searching. With them the orderly marshalling of the ultimate atoms in crystals, indicated by external faces and symmetry, has been proved; the new elements hafnium, masurium, rhenium and illinium have been discovered; the physical properties, practically desirable or undesirable, of such materials as metals and alloys are being fundamentally related to structure; dependable information is being obtained on grain size, purity, solid solution, lattice distortion, internal strains, atomic sizes and shapes, allotropic modifications, valence, density, as these concern crystals; the organic chemist has had the structural theories, upon which his science has been built, directly verified in the X-ray proof of the tetrahedral valency of carbon; of the 6-carbon ring of benzene, taken over from graphite; of the length of long chain compounds; and of the constant effect of adding successive carbon atoms. Thus he finds elegant new methods of determining molecular weights, polymerization, chemical reactivity, isomerism, explanation of optical activity, and the positions of polar groups in molecules.

The analytical chemist has found in X-ray analysis by several methods a new mode of attack. The inorganic chemist has at last discovered the method of establishing such logical relationships as have been the strength of the organic branch of the science, so that he can correctly predict just how the atoms in triammonium heptofluohafniate or other compounds should dispose themselves. The industrial chemist and the engineer are just now awakening to the realization that here is a fundamentally scientific method of research which may solve many of the very difficult directly practical problems of efficient production of commodities, and naturally assist in the development of a vigorous manufacturing technique.

It is but natural, therefore, that the chemist who is primarily in-

interested in the colloidal and amorphous states, in gels, extremely small particles, thin films, etc., should be asking whether X-ray science holds any promise for the problems which confront him, even granting that the extension from the province of the truly crystalline state is *a priori* attended with little promise. It is the purpose of this paper to present briefly an account of the achievements of X-ray researches thus far in the newly tried fields of colloidal and amorphous materials, and thereby to give some indication of what may be hopefully expected in the future. Two distinct types of applications of X-radiation must be at once distinguished, namely, (1) the chemical, physical or biological action of the radiation upon colloidal and amorphous systems, and (2) the utilization of the radiation as a means to structural examination.

II. The Direct Action of X-Radiation:

At the outset it must be stated that present-day knowledge concerning the direct action of X-radiation photochemically, catalytically, or biologically is very limited—far more so than is true for the ultra-violet portion of the electromagnetic spectrum. The number of fundamental investigations is small, because of expense of apparatus, lack of trained research workers, and inherent difficulties involved in using a radiation which is so penetrating. It has been known since the discovery of the rays by Roentgen that they ionize gases; yet there are no quantitative measurements on gases under strictly comparable conditions related to the amount of radiation energy and the liberation of corpuscular rays, which C. T. R. Wilson and the Braggs showed to be the real ionizing agent. If, then, the chemical action of X-rays follows a primary ionization, fundamental data for interpretation are lacking. From a colloidal point of view, the more interesting observations on X-ray action which have been made are as follows:

(1) *The coloration of minerals, salts and glass.* While the violet coloration of glass, etc., has been ascribed to oxidation of manganese, Dauvillier has pointed out that the observable chemical effects of X-rays are always associated with compounds which are known to contain ions—salt crystals, colloids, glasses and even electrolytes. Corpuscular rays, liberated by X-rays, by impact cause negative ions to lose electrons, which are relatively slow moving and neutralize neighboring positive ions. Coloration results from the formation of neutral atoms or even of colloidal particles. In alkali halide crystals the color fades logarithmically with time when removed from the X-ray beam, by a reverse process. The photoelectric and photoluminescent effects and recent measurements of absorption spectra of colored specimens seem to lend weight to this theory of mechanism.

(2) *Photochemical action.* The effect of X-rays on the photographic plate is, of course, familiar in its similarity to light. Instances of positive effect on chemical reactions are very few. Clark, Mead and Cochrane¹ in very careful experiments found that, whereas ultra-violet light or radiation from a Mazda lamp had enormous accelerating effect upon the oxidation of benzaldehyde, rubber and transformer oil, a heterogeneous beam of X-rays from a tungsten target tube operated at 100,000 volts had no photochemical effect whatever. The difficulty involved lies in the failure to absorb the X-radiation. A very hopeful modification of these experiments lies in the use of an admixture of an insoluble inactive colloid, particularly of a heavy metal or its salt. Peskov has already found that colloidal barium salts with diastase increase by twenty-fold the influence of X-rays in diminishing activity. The decomposition of ortho-nitro-benzyl alcohol is similarly influenced. The mechanism involved, of course, is to be found in the absorption of the primary rays and re-emission as secondary rays by the small particles intimately in contact with reacting molecules. Research along this new line in colloidal chemistry promises important results.

Colwell and Russ in 1912 reported quantitative measurements on the transformation of starch sols into dextrin under the influence of X-rays. Because of the entrance of such variables as temperature and hydrolysis, which may produce the same effect, the proof of radiation effect is doubtful and apparently has not been definitely checked by other investigators. The same may be said of the conversions of cane sugar solutions, reported by Fernau.

(3) *Flocculation of colloids.* That there is a definite tendency for X-rays to induce flocculation of colloids under certain conditions seems established. Fernau reported that X-rays coagulate cerous hydroxide and albumin sols. These effects are also produced by hydrogen peroxide and ozone, so that X-rays may cause formation of hydrogen peroxide in the solution, which, upon return to water, liberates electrons which in turn neutralize the positively charged sol. Dognon very recently has reported experiments on gum mastic sols which flocculated when irradiated with a homogeneous beam such as the $K\alpha$ rays from molybdenum. A heterogeneous beam, on the other hand, produced no such effect, indicating some kind of antagonistic effect which seems inexplicable. A careful examination of the original paper discloses no apparent flaw in manipulation or in understanding of filtration.

A beam of general radiation from a tungsten target passed through five identical cells containing the sol and flocculation was greatest in the fifth, although the intensity was 0.01 as great as in the first cell. On the other hand, a monochromatic beam produced

¹ *Proc. Int. Congress of Radiology, London (1925).*

greatest flocculation in the first cell. Such observations, however, require many repetitions and checks against unrayed sols in order to avoid errors in interpretation. If this effect is substantiated it should be of immeasurable importance in the technique of irradiation of biological colloidal systems such as the human body.

(4) *The activation of colloidal catalysts.* This field has been subjected only to a preliminary survey, but the results are of great interest and promise. The oxidation of SO_2 to SO_3 in the presence of colloidal platinum (the so-called sulphuric acid contact process) has been studied recently by Clark, McGrath and Johnson² for a single set of conditions except unrayed and rayed catalyst, and presence or absence of moisture in the gases. The temperatures throughout were 275°C . in the preheating zone and 300° for the catalyst zone. A mixture of 16 cc. of SO_2 and 210 cc. of air per minute was passed over the catalyst. When dried with P_2O_5 the percentage conversion was only 3.25 per cent. Using air in which the ratio of water to air was 0.0130, a conversion of 88 per cent was obtained. After raying the catalyst for 3 hours with rays from a tungsten target tube operated at 100,000 volts, the conversion rose to 94 per cent. This value was maintained for 5 hours and then a rapid drop to 84.5 per cent ensued, followed by a recovery to 87.3 per cent after 9 hours and a slow decrease to a constant value of 84.3 per cent. A second irradiation caused an increase to 87 per cent only, followed by slight evidences of the minimum and recovery noted after the first raying and then the gradual decrease to the same constant value of 84.3 per cent. A third irradiation produces a practically negligible change in conversion. These results are shown graphically in Figure 1.*

The runs made on wet air gave a conversion which was nearly 30 times that obtained when the gases were dried. It would seem almost impossible that moisture could have this effect if the mechanism of the reaction were a simple process, such as the adsorption of the reacting gases and reaction on the catalytic surface. It would seem essential that the moisture forms some compound with the SO_2 which is easily oxidized or some easily reducible oxide with the catalyst itself. The mechanism, suggested by Schwartz and Klingenfuss,³ of the formation of an oxide with the platinum may explain the activation of the catalyst in the presence of moisture. After X-ray activation, probably by ionization, a measurable amount of material is attached to the catalyst, which is reducible by potassium iodide solution. There is actually more oxygen in the platinum catalyst after raying than before.

* *Proc. Nat. Acad. Sciences*, **11**, 646 (1925).

² *Z. Elektrochem.*, **28**, 472 (1922); **29**, 470 (1923).

On the other hand, sufficient data are not yet available to permit an adequate explanation of the sudden drop in activity or "tiring" of the catalyst five hours after raying, with subsequent recovery, or of the decreased effect of raying after the first time. Undoubtedly an adsorbed film of H_2SO_4 on the catalyst is being built up to a thickness which is less easily ionized by X-rays. To the extreme sensitiveness of most catalysts to heat treatment and to poisons, as regards adsorption and activity, must be ascribed these complicated phenomena.

The action here is in several ways strikingly similar to that found by Grube and Baumeister for the changes in potential of anodically

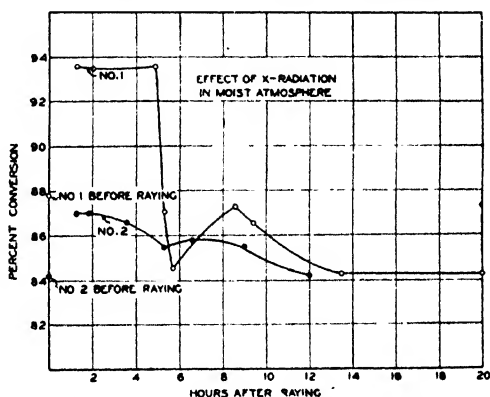
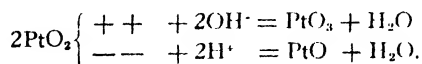


FIG. 1.—Effect of X-radiation in moist atmosphere on conversion of SO_2 to SO_3 .

polarized platinum electrodes under ordinary light and X-rays, both as regards the course of any one curve with time, and the smaller changes with subsequent exposures to radiation. Baur's theory of photolysis may apply in both cases. The effects of a quantum of radiation on a molecule E is expressed as $E + h\nu = E^*$ (active). Then



The changing relationships between these three transient oxides may account for the observed peculiarities.

It is obvious that the present experiments are but preliminary because of the large number of variables involved, which must be investigated: composition of gases, rate of flow, pressure, moisture content, preheating temperature, catalyst temperature, amount of

catalyst, time of raying, X-ray wave-length, runs after or during raying, aging of catalyst, type of catalyst and support, particle size, etc.

(5) *The effect of X-rays on biological colloidal systems.* It has been indicated that in all experiments designed to determine the direct action of X-rays, the variables are difficult to control. In the study of the action of X-radiation on living matter, certainly the most interesting and important both practically and theoretically, the additional variable of life produces complexities which have so far defied satisfactory interpretation. As Dr. James Ewing⁴ in his masterly Caldwell lecture "Tissue Reactions to Radiation" puts it: "Ultimate knowledge of the mode of action of radiation still eludes our grasp." Speaking of action on human tissues, he says "More than a decade ago one could trace in detail the nuclear and cytoplasmic reactions following irradiation, the preliminary hyperemia, cell liquefaction and necrosis, the appearance of phagocytic cells, the growth of granulation tissue, the extreme overgrowth of lymphocytes and plasma cells, the healing by supple scar tissue. . . . The very voluminous contributions of the past decade have served to clarify many details . . . but no new and fundamental principles of reaction have been established." The subject by its enormity and by the vast number of unconnected, largely uncontrolled observations recorded in the literature, ranging all the way from a single cell nucleus to a complete human system, is appalling, particularly in light of the urgent need to have the ultimate knowledge which will permit accurate, scientifically founded, radiation therapy.⁵

In general, the rule holds that small dosages tend to activate and stimulate various functions and chemical reactions in biological colloidal systems, while larger dosages destroy, either instantly or after a latent period. This law has been tested on seeds, eggs, single cells and organisms of every imaginable kind. It has found practical applications in the destruction of tobacco worm larvæ, cotton boll weevil, the flour weevil (*tribolium confusum*), etc. Daily in great hospitals throughout the world cancer patients are being cured or relieved through the agency of X-rays or radium, in spite of the enigmatical phases. As inquiries into the ultimate nature of the action of rays upon tumor and tissue cells become more fundamental in terms of physics and chemistry, they become less satisfying in terms of biology. Such tissues are not merely aggregates of cells but are highly complex systems of related and interdependent structures; purely chemical or physical data can never explain their behavior. And yet it is highly important to review briefly a few of these observations.

First, the cell and nuclear membranes become more permeable.

⁴ *Am. J. Roentgenology and Radium Therapy*, 15, 93 (1924).

⁵ *Cf. Stenström, J. Cancer Research*, 9, 190 (1925).

"The marked swelling of irradiated nuclei and the ballooning of the cytoplasm are most easily and probably correctly interpreted as an increased capacity of these structures to absorb water, through an altered cell membrane. The nature of this cell change escapes us, but again assuming the simplest cause, one must suppose that intracellular chemical changes produce new electrolytes by decomposition of salts, proteins and fats and that water is drawn in by simple osmosis."⁶ One of the gross effects is the actual closing of blood vessels and a disturbance of the vascular supply. Unfortunately there are no simple chemical studies comparing normal with heavily irradiated tissue. Again, radiation inhibits cell ferments. Hussey has shown that simple solutions of pepsin or trypsin are inhibited in action. Theories of splitting of cholesterin, of ionization of cell constituents, of colloid coagulation by points of radiation heat (Dessauer), increase in H-ion concentration, alterations in the dispersion phase, changes in the electric charge of the colloidal constituents, disintegration of lipoids, changes in albumin, increase in the ratio $Q = K(H_2PO_4^- + HPO_4^{2-})/Ca^{+2}$ are among the observations and theories which may be laying the basis for the solution of the problem. Certain it is that tissues must be considered as a whole. "Observations are thus slowly accumulating to show that irradiation, in addition to inhibiting or destroying tumor tissues where the cells have the predominant function of growth, may exert a favorable influence upon the nutrition and metabolism of the body as a whole, may reduce the deleterious effects of the tumor and may possibly cause some non-specific protein immunization (derived from the dying tumor cells and called by Caspari necrose-hormones) which increases the resistance of the body against the tumor, and in favorable cases may throw the balance of nutrition decisively against the unstably nourished neoplasm." In the new joining of research forces to grapple with this great problem, with its manifold ramifications, the colloid chemist must play a great part.

III. X-Rays as a Means to the Study of Colloidal and Amorphous Structure:

While here again a new branch of science must be dealt with, the results so far obtained are considerably more definite and reliable than can be said for the study of direct effects of X-radiation.

(1) *The identification of the states of matter by X-ray diffraction patterns.* It is just now becoming possible by means of X-rays to gain a true insight into the solid state. There exists no longer a

⁶ Ewing, *loc. cit.*
Kroetz, *Biochem. Z.*, 151, 449 (1926).

sharp line of demarkation between crystalline and amorphous states. Present conceptions may be outlined briefly as follows:

Crystalline. In crystals the atoms, ions or molecules are regularly arranged in space in parallel planes, which for any one set all alike are equally spaced. Figure 2 is the photograph of a large model of a sodium chloride crystal. X-rays are diffracted in sharply defined directions as Laue spots or spectral lines. Even powders or aggregates characterized by random distribution of the single crystals

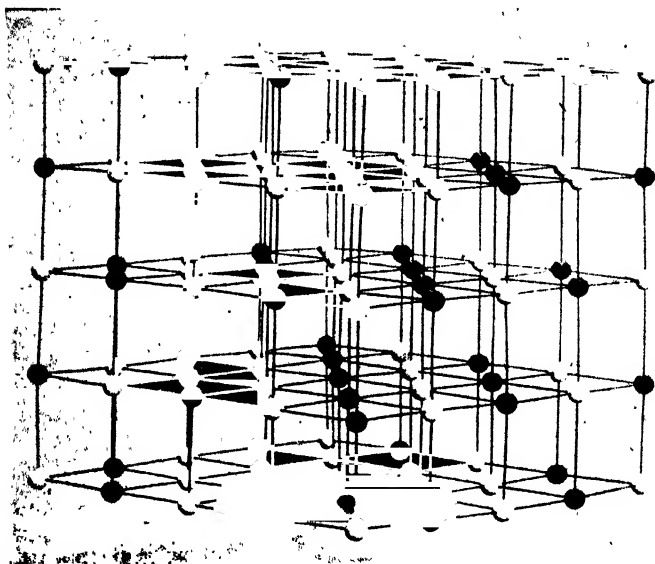


FIG. 2.—Model of crystal of sodium chloride.

or grains produce definite diffraction lines. These are sharp and uniform throughout when the diameter of the diffracting particles lies between 10^{-3} and 10^{-6} cm. If larger than 10^{-3} cm., the diffraction lines become dashed and spotted as would be expected for larger single crystals; if smaller than 10^{-6} cm., the lines become broader in proportion as the particle size decreases in the colloidal range. The equation connecting line breadth and particle size will be considered below. The lower limit of size which will still produce distinguishable though broad powder diffraction lines has not been accurately determined but is the subject of fundamental and quantitative study in the writer's laboratory; certainly particles with a size as small, or films as thin,

as one μ give very satisfactory crystal diffractions, provided, of course, that an undistorted crystal space lattice remains.

Amorphous. In amorphous materials the atoms or molecules are not arranged upon a definite space lattice, nor even in equidistant parallel layers with otherwise perfectly random distribution. The typical diffraction results are general darkening of the film or, usually, one broad diffuse band (sometimes two or three), easily distinguishable from crystal spectra, even from the diffraction effects of colloidal crystalline particles. Liquids, glasses, gels, ordinary unstretched rubber, resins, varnishes, celluloid and allied materials belong to this latter class. The appearance of even a single distinguishable band is, of course, a point of great interest, since it indicates chance formation of lattice structure during thermal agitation of molecules (particularly in liquids), or diffraction by regularly spaced atoms *within* randomly disposed molecules, or formation of molecular aggregates,⁸ or crystal fragments.⁹ De Smedt¹⁰ has shown that the position of these bands is very sensitive to polymerization and that the degree of polymerization can actually be calculated, assuming compact spheres, in the formula

$$\delta = 1.33 \sqrt[3]{\frac{M}{nd}}$$

where M is the simple molecular weight, d the density and n a whole number, representative of the degree of polymerization, which can bring the calculated value of δ into agreement with the experimentally determined spacing $a = 7.72\lambda/4\pi \sin \Theta/2$, Θ being the angle of the diffracted cone of rays. Thus the value of n is 2 for ethyl acetate and butyric acid, and 3 for paraldehyde and benzyl benzoate. These considerations of polymerization are being adapted with interesting results by the writer in the study of polymerized complex glycerides in linseed oil and cumarone derivatives.

Practically all so-called amorphous substances give these crystal-fragment, low-resolution phenomena, but a few give truly amorphous, general scattering, such as liquid mercury, metallic potassium at ordinary temperatures and certain carbon blacks discussed below.

The Mesomorphic State. The recent classical paper by Friedel,¹¹ still far too little known and appreciated, has demonstrated the existence of definite intermediate birefringent states between the crystal, characterized by discontinuous vectorial properties, and the amorphous, characterized by isotropy. His studies were particularly related to those organic substances, largely cholesteryl esters, which form liquid

⁸ Cf. Wyckoff, *Am. J. Sci.*, 5, 455 (1923).

⁹ Cf. Stewart, Morrow, and Skinner. *Am. Phys. Soc.*, November, 1925, meeting.

¹⁰ *Bull. soc. chim. Belg.*, 10, 386 (1924).

¹¹ *J. chim. Phys.* (7), 18, 278 (1922).

crystals. As the temperature of the amorphous isotropic liquid is lowered, there appears discontinuously the nematic state, or the related cholesteric state, in which molecules have a common direction, but no other arrangement, then the smectic state in which the molecules are now also in equidistant parallel layers, and finally the crystalline, in which there is definite arrangement in all directions. Friedel has proved that the nematic state diffracts X-rays just as amorphous, periodicity-lacking substances; the smectic state gives X-ray diffraction lines corresponding to the parallel-layer arrangement. Recent efforts to criticize Friedel's classification based upon results with long chain acids, have been set at naught by Friedel's proof that the substances were truly crystalline in producing side spacings on X-ray films characteristic of molecular cross-sections, in addition to the larger spacing corresponding to length.

The mesomorphic phases, therefore, represent the primary orientation of the molecules in parallel thermal layers in melts or solutions. This results, according to the theory of Rinne,¹² in swarms of minute colloidal crystallites which combine with a growing nucleus to give the completed crystal.

Two new terms will be used to describe the intermediate states which are neither amorphous nor crystalline in the classical sense. These states represent the first tendencies for molecules and atoms to orient symmetrically as to direction and spacing. The *paracrystalline* state is that involving the true, incipient and transition processes which ultimately yield the true crystal with its permanent symmetrical disposition in direction and space. The *metacrystalline* state is a transient symmetrical arrangement of diffracting centers under special external conditions, which is not a transition towards a true crystal. The best example of the metacrystalline state is stretched rubber and gelatine. As will be described later, stretching causes a symmetrical arrangement of molecules in spacing and direction so that X-rays may be diffracted in a manner analogous to that in true crystals; release of the tension on the specimen causes a return to the original condition.

In liquid crystals the long molecules have oriented themselves in their own electrostatic field. A similar result may be accomplished artificially. Molecules of CS_2 , $\text{C}_6\text{H}_5\text{NO}_2$, etc., orient in an electric field (Kerr effect); fatty acid molecules definitely are oriented at interfaces; many adsorption phenomena on catalysts and other surfaces must involve orientation. Remarkable verification is found in recent optical observations by Rinne on adsorbed water in zeolites, layers replaced by alcohol, mercury, etc., and of Frey, who found that dyes impregnating plant fibers and inducing birefringence and

¹² *Naturwissenschaften*, **32**, 691 (1925).

pleochroism are not in the state of small crystals but molecules directed by adsorption forces. Sols of $\text{Fe}(\text{OH})_3$, V_2O_5 , benzopurpurin 4B, etc., are shown optically to undergo definite spontaneous structure formation. These interesting fields are now being subjected to careful X-ray study in the writer's laboratory. Sharp diffraction effects are not to be expected obviously if these paracrystalline layers are only one or two molecules thick. Some experiments with oleic acid in an extremely fine capillary tube indicate very surely that the long molecules are being constrained to parallel layers, for the usual single amorphous band for the liquid in mass becomes noticeably narrower and there are faint evidences of other bands on the photographic film.

Certain carbon blacks display other phases of the paracrystalline state of matter. The transitions here, as also possibly in the very few cases of amorphous solid metals, oxides, etc., occur entirely in the solid state from amorphous to crystalline limits. Debye and Scherrer upon the basis of X-ray examination decided that there were only two modifications of carbon, graphite and diamond, and that so called amorphous carbon was merely graphite in an extremely fine state of subdivision. Clark and Alm, however, agree with Ruff, Schmidt and Olbrich¹³ in that the amorphous state actually is the third modification of carbon and that there is a paracrystalline state between amorphous and crystalline. Certain charcoals and blacks produce only the characteristic amorphous scattering. For some of these even the single broad diffuse band on the X-ray diagram is very ill-defined. These carbons are characterized by high adsorption activity inasmuch as the carbon valences are essentially unsatisfied, a definite solubility in oxidation media, and a definite specific electric resistance. As they are subjected to heat treatment, for example at 1100°C ., the activity decreases, the solubility decreases, and the specific resistance decreases to values corresponding to graphite, but the X-ray diagram remains essentially unchanged. This transition can be followed perfectly through the intermediate stages during heating at high temperatures for varying lengths of time. The considerable lag of the change in X-ray structure behind the change in the physical and chemical properties is evidence of the paracrystalline state, in which by vaporization and diffusion processes, the atoms are becoming linked by valences, but the layers so arranged are still too few, or are so distorted and bent that graphite interference lines are impossible. The amorphous ring, however, tends to become more sharply defined; other bands close to the center begin to appear very faintly as the heating is increased; next, outlying bands corresponding to graphite interferences which have been so diffuse as not to appear visible, define

¹³ *Z. anorg. Chem.*, **148**, 313 (1925).

themselves and then, continuously but very rapidly, the entire graphite spectrum appears. These studies would seem, therefore, a direct evidence of far more continuous transitions between amorphous and crystalline than is true in the apparently discontinuous changes from amorphous fluid to mesomorphic liquid crystal to crystalline solid.

(2) *The X-ray structures of colloids.* It is clear that colloids may give diffraction effects characteristic of crystals, of the intermediate paracrystalline condition, or of amorphous substances. Colloidal metal sols in general give the diffraction patterns characteristic of the massive material, except that the lines are broader in proportion as the particle size is smaller. The outer interferences on a powder diffraction spectrum, which are normally weak in comparison with low-order diffraction lines close to the zero position for densely populated planes, may actually disappear because the energy is spread over greatly widened lines when very small particle size or a paracrystalline condition is reached, while the inner interferences remain visible though greatly diffused. Thus calculation will show that particles containing 5 or 6 carbon atoms will show visibly only the innermost interferences, greatly diffused and characteristic of the paracrystalline condition.

Even gels, rubber, glue, resins and liquids will show a diffraction band which might be identified as the paracrystalline broadening of those interferences which would appear if the material were crystalline. This has certainly been proven by Stewart, Morrow and Skinner¹⁴ for molten and solid naphthalene, α - and β -naphthol, the broad interferences of the liquids persisting to the freezing point.

(3) *The practical determination of crystallinity.* Several interesting researches have established the qualitative value of X-ray diffraction for the study of the conditions of precipitation for true gels or for crystals of a desired size particularly of such hydroxides as aluminium, zinc, calcium, etc. Similarly the X-ray detects with great sensitiveness the aging of gels and the first appearance of any separating crystalline nuclei not discernible by any other method.

(4) *The determination of particle size.* By virtue of the fact that the diffraction lines from crystalline particles with a diameter less than 10^{-6} cm., become broader, Debye and Scherrer were able to derive their equation connecting line breadth with particle size:

$$B = 2\sqrt{\frac{\log e^2}{\pi}} \cdot \frac{\lambda}{D} \cdot \frac{1}{\cos \Theta/2} + b,$$

where B is the angular breadth of a diffraction halo measured between points of half-maximum intensity, Θ is the diffraction angle, λ the

¹⁴ *Loc. cit.*

wave-length, D the average thickness of the crystal parallel to a cubic axis, and b is the minimum breadth determined by the particular apparatus. Debye and Scherrer in this way determined the size of colloidal gold particles as 18.6 A.U., or about 4 to 5 times in any direction the size of the ultimate unit crystal cell of gold.

Clark, Asbury and Wick¹⁵ were the first to make a study of particle size as related to the activity of finely divided catalysts. They measured photometrically the line breadth of diffraction spectra from a number of nickel catalysts, with identical crystal lattice type and dimensions, prepared in various ways, and differing in catalytic activity in hydrogenation and dehydrogenation processes. Most of the catalysts consisted of particles somewhat larger than 10^{-6} cm., and the Debye-Scherrer equation did not hold. In general, increase in activity and decrease in particle size did not run parallel as might be expected, but, within certain limits of size, actually opposite. Thus a catalyst, prepared by reduction with sodium hypophosphite and possessing distinctly the smallest particles in the colloidal range, was relatively inactive.

New unpublished studies by Clark and Aborn, however, on platinum catalysts used in the contact sulfuric acid process, show a more promising relationship between decreasing particle size to an optimum size, with increasing activity. A large number of difficultly controllable variables are concerned since the particle size is determined not only by the metal and by the state as a "black" or a sponge, but by very slight differences in any given method of preparation. Anticipating these results Levi and Haardt¹⁶ have made a beautiful study of particle size of the platinum family of metals from the photometered X-ray diffraction spectra, with the result that the granules of Pt were 12 to 29 times as large on the side as the unit cube; Pd 13 to 29, Rh 6, Ir 4, Ru 7 to 8, and Os 6 (latter two hexagonal). A good automatically registering densitometer is essential to such studies of line breadth. The lower limits in size are comparable with colloidal preparations of the highest degree of dispersion. This type of investigation can be applied with great value to the study of all paints, pigments, dyes, enamels and allied substances. As an example may be shown diffraction spectra of three samples of stannic oxide, SnO_2 . It is interesting that cassiterite, artificially prepared SnO_2 and metastannic acids all yield the same characteristic spectrum for a tetragonal lattice similar to that of rutile, TiO_2 , with two molecules in the unit cell of dimensions $a_0 = 4.72$ and $c_0 = 3.16$ A.U. Figure 3A is the spectrum for one of the samples in which the particle size lies in the diameter range between 10^{-8} to 10^{-6} cm.

¹⁵ *J. Am. Chem. Soc.*, **47**, 2661 (1925).

¹⁶ *Atti. Accad. Lincei* (6), **3**, 91 (1926).

The lines are numerous and so sharp that the $K\alpha$ doublet of molybdenum is easily resolved. The particles are, therefore, of the order of 1000 times as large as the unit tetragonal prism for the oxide.

Figure 3B represents another sample of equal purity but of smaller particle size. Numerous lines are still present but they are broader, the α doublet is not resolved and some of the outermost lines observed in the first sample are no longer visible. It happens that the size here is just below the limit of the range for sharp lines, or about 2×10^{-6} cm. Hence the particles are 50 times as large as the unit prism. Figure 3C represents the practical limit of visible crystalline diffraction. Not more than four very broad lines in the



FIG. 3.—Diffraction spectra of three samples of SnO_2 , showing how particle size affects line width.

position of the most intense SnO_2 interferences are visible. This spectrum has not been microphotometered, but rough measurement and calculation gives a value of D in the Debye-Scherrer equation of about 5×10^{-7} cm. The particles are only about 10 times as large as the unit cell, and hence are comparable with extreme colloidal dispersion. The importance lies in the fact that the opacity and covering power of paints, enamels, etc., varies greatly with the particle size. It is experimentally possible to obtain all possible gradations between the last two spectra, and hence to control the production of SnO_2 for any desired property.

Another interesting field for the study of colloidal particle size is in metals. Martensite, one of the phases of the metastable iron-carbon diagram, always gives broad diffraction lines in the same positions as for pure α -iron (body-centered cubic). So diversified

are the theories concerning martensite that Sauveur¹⁷ has recently collected the opinions of 22 authorities in order to arrive at some common basis. The consensus seems to favor a solid solution of α -iron and carbon. Westgren calculated from his spectra a particle size of 10^{-7} cm., and Wever found 10^{-6} . Very recently, with the assistance of a precision microphotometer, Selyakow¹⁸ has determined the size as 2×10^{-6} cm. He has followed also the effect of heat treatment in narrowing the diffraction lines and causing the appearance of cementite, Fe_3C at 625°C . Clark and Brugmann in studying the structure of case hardened steel, which is martensite



FIG. 4.—Pinhole diagram of case hardened steel showing very small grain size.

and troostite very largely, found the characteristic very broad diffuse diffraction bands, indication of a particle size nearer 10^{-7} than 10^{-6} cm. A typical X-ray pinhole diagram is shown in Figure 4. Lucas has observed under his ultraviolet microscope that even troostite appears as a perfectly homogeneous mass indicative of subultraviolet crystal size, except for faint evidences of crystalline form at grain boundaries under polarized light.

Clark, Brugmann and Kaufmann have recently devised an apparatus for taking X-ray diffraction photographs of surfaces.¹⁹ A photograph of the apparatus is shown in Figure 5. A beam of X-rays defined by pinholes impinges upon the surface of the specimen on the central mounting which can be inclined to a definite

¹⁷ *Trans. Am. Inst. Mining Met. Eng.*, 1926.

¹⁸ *Trans. Phys. Tech. Lab. Leningrad*, 100, 34 (1925).

¹⁹ Announced at Tulsa meeting of the Am. Chem. Soc., Apr 1926.

angle of incidence, Θ . Automatically the flat film cassette is inclined at 2Θ so that the diffracted X-rays will fall normally upon the film. By varying the angle of incidence it is possible to secure different degrees of penetration into the specimen. In Figure 6 is shown the structure when a beam barely grazed the surface of a worked duralumin specimen. The diffraction rays are so broad that they



FIG. 5.—New apparatus for study of surface reflections

practically merge into each other. Hence the outermost grains have been broken up into particles of colloidal dimensions and probably distorted in the rolling process. The theory of amorphous metal on rolled surfaces is, therefore, not so visionary as recent investigations might indicate. A slightly greater angle of incidence brings out the typical sharp rings characteristic of grain size in the interior metal only a very few atom layers below the surface, as shown in Figure 7. With this simple apparatus remarkable results are being obtained on surfaces and very thin films of many kinds.



FIG. 6.—Diffraction photographs of rolled duralumin sheet taken on apparatus in Figure 5 with 5° grazing angle of incidence; distortion and breaking up of grains on surface are indicated.



FIG. 7.—Same as Figure 6 excepting that the angle is 25°. Note regular reflections from well-defined interior crystals.

Davis and von Nardroff²⁰ have recently presented a mathematical relationship depending upon *refraction* by small particles, which may be of great importance in the range of particles between 10^{-3} and

²⁰ *Am. Phys. Soc.*, April, 1926, meeting, Washington, D. C.

10^{-6} cm., not otherwise measurable. They find experimentally upon their rocking spectrometer an effective particle size in a sample of graphite of 3.5×10^{-3} cm.

(5) *The structure of rubber by X-ray analysis.* For more than a year and a half the writer has been using X-ray methods in the

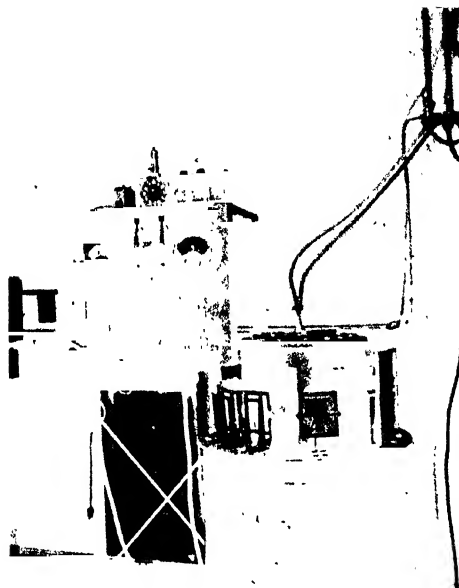


FIG. 8. New Multiple X-Ray Spectograph combining the powder diffraction and monochromatic pinhole method.

investigation of the fundamental ultimate structure of rubber and allied substances.²¹ The detailed observations have not been published. Recently, however, several papers by J. R. Katz²² have appeared, which report the results of comprehensive experiments on the structure of rubber as revealed by X-ray examination. The essential results have been confirmed both in the writer's laboratory and by Hauser and Mark.²³ The pinhole method, with X-rays of a

²¹ Clark, *Am. J. Roentgenology and Radium Therapy*, 12, 556 (1924).

²² *Chemische Z.*, 49, 353 (1925); *Naturwissenschaften*, 30, 410 (1925); *Z. angew. Chem.*, 38, 439, 545 (1925); *Kolloid-Z.*, 36, 300; 37, 19 (1925).

²³ *Kautschuk*, December, 1925, p. 10.

single wave-length from a copper target X-ray tube, has been used to best advantage by all investigators on rubber. The new multiple monochromatic pinhole apparatus used in the writer's work is shown in Figure 8. It has been fully described in a recent paper.²⁴

The structure of ordinary rubber. Any sample of pure Hevea or vulcanized rubber produces the X-ray diagram typical for an amorphous material, i.e., a single broad diffuse ring. Such a diagram is shown in Figure 9. This fact has of course been known for several years.



Fig. 9.—X-Ray Spectrum of pure unstretched rubber.

Crystalline material in raw rubber. Many samples of rubber before mechanical or heat treatment contain crystalline material. This is proven by the presence of practically continuous concentric rings (Debye-Scherrer-Hull), indicating also random arrangement, in addition to the amorphous band. Katz reports the following results:

Yellow crepe	Crystal interferences	good
Thick white crepe (shoe soles).....	"	"
Light brown crepe.....	"	"
Ribbed smoked sheets.....	"	very good
Raw para rubber, washed and dried.....	"	doubtful
"Patentgummi," light yellow unvulcanized....	"	good
"Patentgummi," brown unvulcanized.....	"	excellent
Dried latex	"	none

These crystalline ring interferences on the films disappear when the rubber is masticized or heated and do not reappear. They remain when the raw rubber is stretched even to a large per cent extension. Hauser and Mark have been unable to discover crystals in

²⁴ Clark, Brugmann, and Aborn, *J. Optical Soc. Am. and Rev. Sci. Instrs.*, 12, 379 (1926).

any of their samples of raw rubber, and Clark and associates have found only doubtful evidence in one or two cases.

Pummerer and Koch²⁵ have been able recently to isolate colorless and comparatively non-elastic crystals from smoked sheets by repeated extractions and purifications. The analysis of the crystals indicated pure C_8H_8 . An X-ray powder diffraction spectrogram had lines corresponding to a monoclinic crystal lattice and a unit crystal cell of the dimensions $4.83 \times 4.71 \times 5.33 \times 10^{-8}$ cm., and an angle between axes of $77^\circ 19'$. The cell contained only one molecule of C_8H_8 , as calculated from the volume of the cell and the density of the crystals (0.94). In several trials Clark and associates have been unable to duplicate this work.



FIG. 10.—X-Ray spectrum of pure rubber stretched 500 per cent.

Effect of freezing rubber. Katz, as well as others, has attempted to cause rubber to crystallize at low temperatures. All efforts so far have failed to produce any change in a product which gives the amorphous X-ray diagram. The results of experiments by Simons and Simson who are subjecting rubber to temperatures of -183° C. for some time, will be awaited with interest.

The effect of stretching rubber. This effect is by far the most important of all those observed. In all cases when the rubber is stretched, the X-ray diagram shows a marked change. In addition to the amorphous ring which is always evident, but decreases in intensity with increase in elongation, there appear definite interference spots, which become sharper and more distinct the greater the stretching, but retain the same position. Pure Hevea rubber must

²⁵ *Liebig's Ann.*, 438, 294 (1924).

be stretched about 75 per cent before the crystal-like spectrum appears. From here on to the breaking point the specimen produces a *pure fiber diagram* with the spots lying on hyperbolas as shown in Figure 10. There is no tendency for the spots to merge into the rings characteristic of random arrangement. Hence, here is a case of the appearance during the stretching of metacrystalline diffracting material, all arranged parallel with respect to the direction of the applied tension. The exactness is indicated by the fact that the spots lie on hyperbolas as they should for perfect fibers.²⁰ The interference points resemble those caused by true crystals in that the sines of the half-angular distances from the primary ray increase proportional to the wave-length. Thin, strongly stretched threads of pure rubber show crystal interferences of an intensity comparable with that obtained with pure organic compounds. Control researches with purest rubber, free from resins and foreign inclusions, show the structure, hence it may be concluded that the hydrocarbon (C_5H_8) is actively concerned.

Vulcanized rubber must be stretched as much as 250 per cent before the fiber structure appears. In this case the diagram at first approaches Debye-Scherrer-Hull rings with strong localized maxima, indicating incompletely perfect orientation of the units. Most synthetic rubbers act similarly, although some break before they can be stretched sufficiently. Clark and Lanyon have found that the percentage elongation required to produce a good diagram depends very markedly upon the previous history and composition of a sample, some requiring as much as 800 per cent increase.

The entire phenomenon is reversible if the specimen is not too strongly stretched; that is, upon releasing tension the amorphous diagram is again obtained. In some cases evidences of fiber structure are still apparent a half hour or more after the release of tension, particularly when the specimen does not shorten to its original length.

The nature of the crystals. The question which naturally occurs is whether this metacrystalline material existed before the stretching. It might be possible that the interferences are weak because they are distributed over the entire 360° of the circular X-ray diagram, whereas they are concentrated into small easily visible arcs upon stretching. However, all the evidence seems to support the contention that the crystals do not exist as such, prior to the stretching. When raw rubber which is partially crystalline even unstretched, is stretched, new interference maxima appear on the already apparent circles which persist even with the greatest tension. The latter disappear upon warming but the fiber diagram reappear upon weakly stretching the sample. Unstretched rubber is amorphous; stretched rubber has two constitu-

²⁰ Polanyi, *Naturwissenschaften*, 9, 880 (1921).

ents, metacrystalline and amorphous. Molecules or elementary units of an associated molecule in preformed swollen aggregates may arrange themselves regularly by virtue of the tension, and thus produce the metacrystalline condition.

The lattice dimensions. Measurements by Katz of the X-ray interferences of all the stretched rubber samples indicate a unit crystalline cell of the approximate dimensions $8 \times 6\frac{1}{2} \times 6\frac{1}{2} \times 10^{-8}$ cm. Hauser and Mark's values, for an orthorhombic unit cell containing 8 molecules, are $8.0 \times 8.6 \times 7.68 \times 10^{-8}$ cm. This is very small when the polymerized rubber molecule as usually visualized is considered. The unit cell has been heretofore always associated with at least one molecule; in rubber and cellulose each cell contains only a portion of a polymerized molecule. These portions must be all alike and held together in the aggregate by secondary valence forces.

Ott²⁷ has recently found a specimen of crepe rubber which yielded sharp interferences. The innermost of these, as is always the case in powder diffraction spectra, corresponds to the largest spacing in the unit cell, and for X-rays from an iron target, has an angle of incidence in $n\lambda = 2d \sin \Theta$ of $8^\circ 42'$. The value of d is therefore 6.37 A.U. or the volume of the largest possible cell, δ^3 , is 259 A.U.³ These values are almost exactly checked on films taken by Clark and Langen. Taking the Bragg values for the radii of $C = 0.77$ A.U. and $H = 0.73$ A.U., and assuming close packing, the volume of C_5H_8 would be $5 \times (2r_c)^3 + 8 \times (2r_h)^3 = 18.26 + 24.88 = 43.1$ A.U.³ The determination of the maximum volume is therefore six times as large, or in other words, the maximum formula for rubber is $(C_5H_8)_6$.

The effect of fillers and inorganic mixtures. Rubber mixtures containing sulfur, zinc oxide (ZnO), magnesium oxide (MgO), lead oxide (PbO), ferric oxide (Fe_2O_3), barium sulphate ($BaSO_4$), mercuric sulfide (HgS), graphite and magnesium carbonate ($MgCO_3$) show the typical fiber diagram for rubber when stretched. In addition all give rise to the Debye-Scherrer-Hull rings characteristic for the finely powdered inorganic constituents of the mixture. The grains of magnesium carbonate alone, under normal circumstances, show any tendency to assume a fiber arrangement during stretching, for above 300 per cent extension the magnesium carbonate rings become disconnected arcs. This method of examination should prove very fruitful in determining the size, properties, and chemical combinations of the added inorganic substance after vulcanization, by comparison with the X-ray diagrams of the pure substance.

X-ray structure and physical properties. The facts brought out by the X-ray examination explain those physical properties which so peculiarly characterize rubber. During stretching for the first 75 per

²⁷ *Naturwissenschaften*, 15, 320 (1926).

cent in pure rubber a gel substance characterized by small fluidity and large elasticity predominates. From this on threads or meta-crystals of a strongly cohesive and much less ductile substance account for the much smaller elongation for a given force before breaking. The effect discovered by Joule in 1857, that rubber heats upon being stretched while other substances cool, is explained by the heat of crystallization. Upon the basis of the X-ray structures the material might be expected to cool in the first stages of stretching. Joule found that this was indeed true for rubber. The recent remarkable researches of Freundlich and Hauser²⁸ with the micromanipulator have shown that the latex particles have an inner milky portion which becomes hard upon vulcanization, and an outer polymerized skin. These must be responsible, respectively, for the amorphous and the crystalline parts of the X-ray diagrams. The present writer has found that all hard rubbers indeed are amorphous in their ordinary state.

6. *Balata and gutta percha.* In unpublished studies carried on a year and a half ago on the structure of balata, a coagulated latex similar to rubber, and often used with it, Clark and Brugmann found it to be distinctly crystalline under all conditions, although some amorphous material is also present. The commercial, unstretched, uncalledered material produced several concentric rings of uniform intensity indicative of chaotically arranged crystals. This structure was retained after careful extraction of the material. With a specimen to photographic film distance of 10 centimeters the following measurements were made on the easily visible rings.

No.	Distance on Film	Tan 2 θ	θ	λ	d
1	1.17 cm.	0.117	3.34°	0.71	6.10
2	1.35	0.135	3.85°	0.63	4.61
3	1.57	0.157	4.46°	0.71	4.58
4	1.90	0.190	5.40°	0.71	3.77
5	2.35	0.235	6.62°	second order	of 1
6	2.70	0.270	7.55°	"	" " 2
7	3.15	0.315	8.80°	"	" " 3

It will be observed that the largest spacing is approximately the same as that for rubber. Hence the formula $(C_6H_8)_n$ must also represent the maximum unit cell formula for balata. When balata is stretched hot or cold, 50 per cent, the diffraction diagram changes from circles to symmetrically arranged arcs characteristic of a fiber and of rolled or drawn metals, but the spacings remain unchanged.

Ott has recently taken diffraction photographs of gutta percha. This is definitely crystalline like balata and the largest spacing is 8.12 A.U. Calculating as for rubber, the maximum number of molecules of C_6H_8

²⁸ *Kolloid-Z.*, **38**, 15 (1925).

in the unit cell is 12; in other words gutta percha is fundamentally $(C_6H_8)_{12}$.

7. *Gelatin, Collagen, and Glue.* It may be predicted that all substances which shorten when they are warmed in the stretched condition, such as gelatin, glue, muscle fibers, etc., should display X-ray phenomena similar to rubber. Clark and Lanyon have found that pure, ashless, isoelectric gelatin unstretched produces a broad "amorphous" ring corresponding to a spacing of slightly less than 4 A.U. and an outer sharp ring related to a crystalline spacing of 2.79 A.U.

Katz and Gerngross²⁹ have verified the prediction for stretched gelatin and Herzog and Gonell³⁰ for collagen (gelatin minus water). For a pure, ashless, isoelectric gelatin gel the former obtained a diagram which agrees exactly with that independently observed by Clark and Lanyon. When stretched 50 per cent the sharp circle became merely two unconnected crescents in the stretching direction, showing the preferred orientation of the crystals originally present. At 100 per cent elongation larger elliptical intensity maxima appeared on the film perpendicular to the stretching direction, one pair joined to the central direct beam and corresponding to a spacing of 10 A.U. and the other pair on the inner side of the broad "amorphous" ring corresponding to $5\frac{1}{2}$ A.U. These are connected with the arrangement of diffracting parallel layers during stretching. Almost identical results were obtained from fibrous collagen (tendon of Achilles).

Herzog and Gonell studied apparently unstretched collagen from six separate and widely varied sources, including three from connective tissues and three from cartilage. The diagrams for all except fish scales were cloudy, showing the presence of amorphous material with the crystalline. In some cases digestion with trypsin solution removed the amorphous material leaving the crystalline. The crystalline component of all the collagens gave exactly the same diagram. The elastin from the neck ligament of cattle thus appears identical with collagen. The interference bands are not numerous enough to establish the crystal system. It is clear, however, that the mass per unit cell must be far less than that corresponding to such formulas as $C_{35}H_{57}O_{18}N_{11}$ (Proctor) or $C_{32}H_{52}O_{12}N_{16}$ (Wilson). Thus a molecule occupying an elementary cell of a collagen crystal cannot contain all 13 of the amino acids found in gelatin. Most of the amino acids, therefore, appear to be present as the amorphous impurities. A unit cell of maximum dimensions corresponding to the strong crystalline diffraction line (2.79 A.U.) would contain even less than so simple a molecule as C_5H_5ON (roughly the Proctor molecule divided by 11).

Clark and Lanyon have studied glues and found the ashfree ma-

²⁹ *Naturwissenschaften*, 44, 901 (1925).

³⁰ *Ber.*, 58B, 2228 (1925).

terial practically identical with gelatin in that the X-ray diagram shows an amorphous band (identity period 4 A.U.) but different in that outlying sharp crystalline lines, characteristic of isoelectric gelatin, never appear. Stretched samples (glue and glycerin printing roll mixtures) also behaved as stretched gelatin. Space does not permit tabulation of the large number of varied experiments on the structure of glue. Adhering films of glue showed no property essentially different from those of blocks of the material. It may be safely concluded that adhesion is a mechanical solidification of the gel around and upon minute fibers. This is borne out by photomicrographs of great magnification.

Varnishes, waxes, etc. Shellac has been found to be distinctly crystalline, for the diagram is a series of concentric sharp circles for a fundamental spacing of 3.67 A.U. Polymerization during heating may be followed perfectly, for the crystalline diffraction rings gradually disappear, and the intensity of a broad "amorphous" band increases. Clark and Aborn, working with dried linseed oil films, found usually a characteristic broad diffuse band, but under certain conditions of extreme oxidation numerous broad bands and sharp crystalline lines of great significance. The crystals seem to be in very thin layers. These results will be reported in detail after further careful work. New experiments have verified the crystalline nature of greases, paraffin, soaps, fatty acids, etc. Clark and Graves have made the first careful measurement of the side spacings for the unit cells in commercial paraffins. There is a definite increase in these values (4 to 6 A.U.), for the cross-section of the cells containing the long carbon chains, with increase in melting point of the paraffin waxes.

Most of the resins from coal tar produce only a single broad band, whose position, however, is very sensitive to polymerization. Those which are unsatisfactory in practical service in varnishes, etc., contain distinctly crystalline material which can be detected easily by X-ray analysis. Upon the basis of these observations further quantitative studies relating structure to physical properties are being made. Natural resins invariably contain both amorphous and crystalline matter.

8. *Cellulose.* Space does not permit adequate presentation of all the information which has been obtained on the X-ray analysis of cellulose. The outstanding results in more or less chronological order may be briefly enumerated as follows:

(1) C. von Nageli many years ago found that cellulose has the property of doubly refracting light; hence cellulose possesses some crystal structure.

(2) This property has been confirmed by X-ray investigation in natural fibers, celluloses precipitated from various dispersions (viscose, etc.) and their fibers most recently in the studies of Clark, Lanyon,

Freudenthal and Kulp on cotton, wool, silk, hemp, sisal, ramie and all varieties of rayon.

(3) The acetyl derivatives of cellulose can be crystallized from their solutions into very definite crystals with faces.

(4) Debye and Scherrer obtained X-ray interference diagrams from cellulose in 1916, confirming indications from (1), (2) and (3).

(5) Herzog, Jancki and Polanyi showed that celluloses from different sources produce interferences for the same crystal system and same axial ratios.

(6) Herzog, in careful evaluation of Debye-Scherrer diagrams, found the axial ratios to be $0.6935:1:0.4467$. Therefore, the crystal cell belongs to the rhombic system.

(7) Herzog with the monochromatic pinhole method proved that cellulose powder produces diffraction rings; with the beam parallel to the length, fibers show diffraction rings; and with the beam perpendicular to the length of the fibers they show the fiber diagram. The conclusion is that cellulose fibers consist of crystallites joined end to end throughout the length of the fiber.

(8) Depending on the previous treatment, either mechanical or chemical, so does the diagram vary.

(9) Herzog and Jancke evaluated the dimensions of the elemental cellulose body as $7.9 \times 8.45 \times 10.2$ A.U., the calculated number of $C_6H_{10}O_5$ molecules composing the elemental cell is 4.

(10) Mark and Katz found that mercerized cellulose no longer shows a cellulose spectrum but new bands are manifested. There is no change in relative intensities of maxima, and amorphous rings appear, all indicating the formation of a new compound.

(11) With very pure cellulose the original diagram disappears at the same alkali concentration as breaks in Vieweg and Heuser's alkali adsorption curves, corresponding to the formation of $(C_6H_{10}O_5)_2$ NaOH and $(C_6H_{10}O_5)_3$ NaOH.

(12) These new bands occur at the same places whether the alkali is NaOH, KOH or LiOH. There is a possibility, therefore, of conversion of the cellulose to an isomer by the alkali.

(13) A similar change occurs with HNO_3 , but not with HCl or H_2SO_4 . There is an open question as to the possibility of "cellulose hydrate" formation.

(14) Sodium hydroxide-alcohol-water solution gives the same changes as sodium hydroxide-water solution, but the strength of the alkali in the former case causing disappearance of the original diagram does not check the alkali adsorption curves for sodium hydroxide-alcohol-water solution.

(15) When regenerated by thorough washing, cellulose gives the original cellulose diagram, with the lattice enlarged about 4 per cent,

and a new band. There is, therefore, only a partial reversion of the swollen material to the original cellulose.

(16) No measurable differences are noted in the space lattice of swollen and unswollen cellulose, hydrated cellulose and artificial silk fibers. Swelling is clearly due to imbibition of water between the unit cells.

(17) Freudenthal and Kulp, working with the writer, have established the fact that all cellulose is crystalline except the diacetate rayon which is amorphous. The degree of fibering, however, varies widely from a minimum in viscose to a maximum in natural fibers, particu-



FIG. 11.—X-Ray diagram of ramie fiber.

larly ramie, whose diagram is shown in Figure 11. Tension on the fiber and the solution dispersion in rayon production have large effects upon the fibering as disclosed by X-ray diffraction.

(18) In this investigation also it has been found that the impurities are an integral part of the cellulose crystals. Pectins, rosins, etc., incidentally present, do not effect the diagram; the integral impurities are degraded celluloses. Profound changes in intensities of the X-ray diagrams following purification with 1 per cent sodium hydroxide solution are not clearly understood. However, these observations place serious doubts on the picture of the cellulose crystal units embedded in waxes, rosins and pectins.

(19) The largest spacing observed in common on all cellulose diagrams was 5.7 A.U. A maximum cell is therefore d^0 or 185 A.U. Cal-

culating the volume for one $C_6H_{10}O_5$ residue from Bragg radii values of 0.77 for Carbon, 0.73 for Hydrogen and 0.65 for Oxygen gives 64 A.U.³ Hence a maximum unit cell formula is $(C_6H_{10}O_5)_3$, in spite of Herzog's dismissal of the value of 3 as impossible. It is interesting to note that the spacing corresponding to the strongest intensity maxima on all the fiber diagrams is 4.0 A.U. A unit cell built with this dimension would hold exactly one $C_6H_{10}O_5$ residue with the atoms filling all the space. Again it must be emphasized that the X-ray data differs by its very nature from physical or chemical estimates of molecular or polymer size in cellulose, rubber, gelatin, etc. In every case the unit crystal cell is far simpler than anticipated. This means either that the real molecules are simpler but appear in macroexamination colloidal or



Fig. 12.—Structure of electrodeposits of lead from fluoroborate electrolytes; A without one per cent gelatin; B with one per cent gelatin.

secondary valence aggregates, or that there are structural periodicities within large loosely bound molecules which diffract X-rays as if there were layers of discrete molecules.

(20) Ott³¹ has recently made beautiful pinhole photographs of cellulose and substances all related to the dehydrated glucose residue. The essential results are as follows:

Substance	Probable Formula	Maximum Spacing	Probable Maximum Unit Cell Formula
Diamylose	$(C_6H_{10}O_5)_4$	11.35 A. U.	$(C_6H_{10}O_5)_{22} ?$
Tetramylose	$(C_6H_{10}O_5)_4$	9.02	$(C_6H_{10}O_5)_{12} ?$
Octamylose	$(C_6H_{10}O_5)_8$	15.96	$(C_6H_{10}O_5)_{68} ?$
Triamylose }	$(C_6H_{10}O_5)_6$	7.27	$(C_6H_{10}O_5)_6$
Hexamylose }			
Inulin		7.34	$(C_6H_{10}O_5)_8$
Cellulose	$(C_6H_{10}O_5)_4$	6.01	$(C_6H_{10}O_5)_3$
Lichenin		7.69	$(C_6H_{10}O_5)_7$
Starch	$(C_6H_{10}O_5)_2$	5.21	$(C_6H_{10}O_5)_2$

³¹ *Physics* 2, 27, 174 (1926).

(7) *Effect of colloids on X-ray structure of electro-deposited metals.* The effect of small amounts (1 per cent) of gelatin, glue and related gels on the structure of electrodeposited metals is most eloquently shown in Figures 12A and 12B, taken from the paper by Frölich, Clark and Aborn on Electrodeposited Lead.³² In both cases all conditions were identical, fluoborate electrolyte, concentrations, current density, temperature, etc., except that in one, 1 per cent gelatin was added. 12A without gelatin shows large crystals, indicated by the discrete large spots; 12B with gelatin shows fine structure rings of uniform intensity. The trace of colloid has resulted in a great diminution in grain size and, from the standpoint of uniformity and cohesion, a film infinitely superior to the deposit from an electrolyte without gelatin.

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Trans. Am Electrochem Soc (1926)

THE STRUCTURE OF RAMIE CELLULOSE AS DERIVED FROM X-RAY DATA ¹

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From time to time during the last few decades, various constitutional formulæ have been proposed for cellulose, most of which have been supported by chemical evidence; but the recent researches of Irvine² and his associates have furnished grounds for the rejection of practically all of these, since none of them can be reconciled with the observation that cellulose, upon methylation and subsequent hydrolysis, yields 2, 3, 6 trimethyl glucose as its sole product. The formula proposed by Irvine and several related formulæ suggested by him³ and by others,⁴ are consistent with the above observation and apparently account for the chemical reactions of cellulose.

It has long been recognized, however, that a satisfactory formula for cellulose must account for its physical properties as well as for its chemical reactions. In this connection, we quote the words with which Irvine and Hirst open their paper on "The Molecular Structure of Cotton Cellulose":⁵ "It will be generally admitted that a complete study of cellulose must include, in addition to purely chemical inquiries, physical investigations on the mechanism whereby discrete particles are arranged to form organized structures possessing the properties of fibers." None of the structural formulæ so far proposed has afforded an explanation of the fibrous nature of cellulose nor of its physical behavior. When it is considered how much of the nature of cellulose is bound up in its fibrous structure, its tensile strength and the swelling behavior that it exhibits, it is seen how inadequate are formulæ which explain only its chemical reactions and leave its physical properties untouched.

Based upon X-ray data recently published, the present authors have arrived at a conception of the structure of cellulose which seems to be

¹ This paper is a joint contribution from the Department of Botany, University of California, Southern Branch, Los Angeles, Calif., and the Division of Plant Nutrition, University of California Agricultural Experiment Station, Berkeley, Calif.

² Irvine and Hirst, *J. Chem. Soc.*, 121, 1585-91 (1922); 123, 518-32 (1923); 125, 15-25 (1924); Irvine, *Chem. Reviews*, 1, 47-71 (1924); *J. Soc. Chem. Ind.*, 41, 362R-363R (1922).

³ Irvine, *J. Soc. Chem. Ind.*, 41, 363R (1922).

⁴ Hibbert, *J. Ind. Eng. Chem.*, 13, 256-60, 334-342 (1921); Hess, *Liebig's Ann.*, 434, 1-144 (1923); Schorger, *J. Ind. Eng. Chem.*, 16, 1274-5 (1924); Herzog, Karrer, see Heuser, West and Esselin, "Textbook of Cellulose Chemistry," 195 (1924).

⁵ Irvine and Hirst, *J. Chem. Soc.*, 123, 518-32 (1923).

in accord with its known chemical reactions and physical properties.⁶ From those investigations,⁷ carried out on ramie fibers which are composed of practically pure cellulose, a space lattice with the following characteristics was determined:

1. The constituent building units are arranged in continuous parallel chains which run lengthwise of the fiber.
2. These chains are spaced rectangularly 6.10 by 5.40 Å. u. apart.
3. The component parts in each chain are repeated every 10.25 Å. u.
4. The elementary cell, therefore, may be thought of as having the dimensions 6.10 by 5.40 by 10.25 Å. u.
5. In this elementary cell, that is, within the spacing of 10.25 Å. u. on each chain, there occur two C_n units.
6. Within this elementary cell, the atoms are so arranged that a number of planes occur whose spacings bear simple numerical relations to the 10.25 dimension; that is, there are sets of planes whose interplanar spacings are 5.15, 3.40, 2.58, etc.

Figure 1 shows in perspective a space lattice having these specifications. The vertical lines represent the center lines of parallel continuous chains of units and the spacing of these chains with respect to each other is indicated by the dotted lines. In a single elementary cell of the lattice, indicated by the dimension figures, only two sets of planes, 5.15 and 3.40, are shown.

From this X-ray data alone, it is possible to gain little more than a conception of the spatial relation between the groups and to obtain a clue, at least in one direction, as to the internal arrangement of the atoms within the group. This becomes evident when it is recalled that the C_n unit, which acts as the unit of structure of the lattice, consists of 21 atoms. This large group of atoms, acting as the unit of structure in the fiber, is in a sense comparable to the single atom structural unit of the simpler crystal forms, such as sodium chloride. It was accordingly possible to ascertain the spatial positions of the unit groups with considerable certainty, but in contrast to the simpler structure of sodium chloride, it was not possible to determine accurately the relative positions of the atoms within the C_n group. In order, then, to obtain a more intimate knowledge of the relative positions of the atoms, it was neces-

⁶ In a recent publication (*J. Phys. Chem.*, **30**, 455-67 (1926)), R. O. Herzog has revised, somewhat, an earlier interpretation of his cellulose lattice and has attempted to reconcile certain physical properties and chemical forms with the revised structure. His data seem to be in fair agreement with ours but his interpretation, we feel, is inconsistent with the data he presents. While we do not feel that we should enter into a discussion of his interpretation in the present article we do feel obliged to point out certain discrepancies in defense of our own interpretation of the X-ray patterns. He has mentioned that several of his interference points do not fall within the limits of experimental error and has assumed these discrepancies due to impurities in the cellulose. These points, however, are classed as strong and medium in intensity. That would indicate a large percentage of impurity which does not seem consistent with the composition of such fibers as cotton, ramie, etc. If large amounts of impurities are not present, then all of the interference points should be explained by the lattice.

⁷ Sponner, *J. Gen. Physiol.*, **9**, 221-233 (1925); *J. Gen. Physiol.*, **9**, 677-695 (1926).

sary in the present investigations to use other types of evidence along with the X-ray data.

In an earlier paper,⁸ the agreement between the volume of the elementary cell as given here and the volume of the $C_6H_{10}O_5$ group of

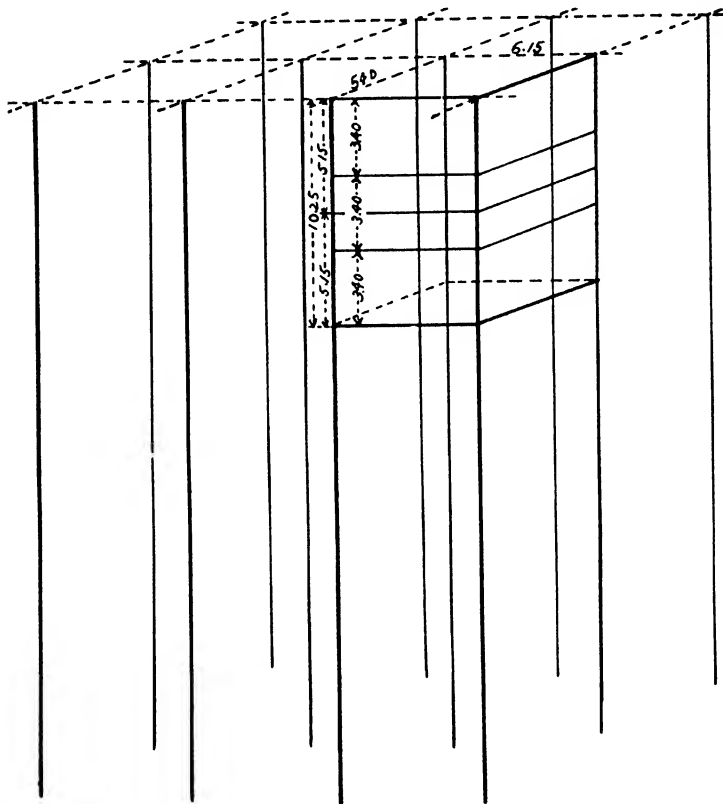


FIG. 1.—Perspective view of cellulose space lattice. Vertical lines indicate positions of center lines of chains of units. A single elementary cell is represented in upper right hand corner, with several transverse planes.

cellulose was pointed out. Since it is now definitely established that cellulose is made up solely of glucose units,⁹ the ascertained space lattice for ramie cellulose must be produced by some arrangement of glucose units or of their condensation products. The problem of discovering

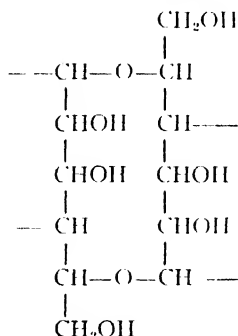
⁸ Sponsler, *J. Gen. Physiol.*, **9**, 221-233 (1925).

⁹ Irvine and Hirst, *J. Chem. Soc.*, **121**, 1585-91 (1922).

the cellulose structure was, accordingly, resolved into two parts, namely, (1) ascertaining which of the several possible glucose structures is involved, and (2) determining the arrangement of the glucose units in the cellulose structure.

Selection of the Glucose Unit.

Of the various glucose formulae that come into consideration as possible structural units of cellulose, we may immediately reject the open chain aldehydic structure, since cellulose fibers normally show negligible aldehydic reactions, and consequently cannot be made up of units which contain active aldehyde groups. The possibility would remain that the structural units are straight chain, non-ring units in which the potentially aldehydic carbon atom is linked by an oxygen bridge to a carbon atom in another similar glucose unit, as in the constitutional formula proposed by Schorger.¹⁰



This conception must also be rejected, however, since the C-O-C linkage would require a rectangular spacing of 2.75 Ångstrom units between chains, calculated from the sum of the atomic radii involved, whereas the X-ray data indicate definitely that the spacing between chains is 6.10 Ångstrom units in one direction and 5.40 in the other. Further grounds for the rejection of both straight chain formulae are found in the fact that a chain of six carbon atoms when fully extended cannot be accommodated in the available spacing allowed by the X-ray data.

Turning, then, to ring formulae which involve the first carbon atom, only two of the five conceivable formulae require consideration, namely, the 1-4, or butylene oxide ring, and the 1-5, or amylen oxide ring structure. The three remaining ring formulae are highly improbable

¹⁰ *J. Ind. Eng. Chem.*, **16**, 1274-5 (1924).

on stereochemical grounds; furthermore, carbohydrates containing such rings have not been found in nature. The possibility of their occurrence in cellulose appears to be definitely excluded by the methylation studies of Irvine and his associates,¹¹ which show that the second, third and sixth positions are occupied by replaceable hydroxyls, consequently ring

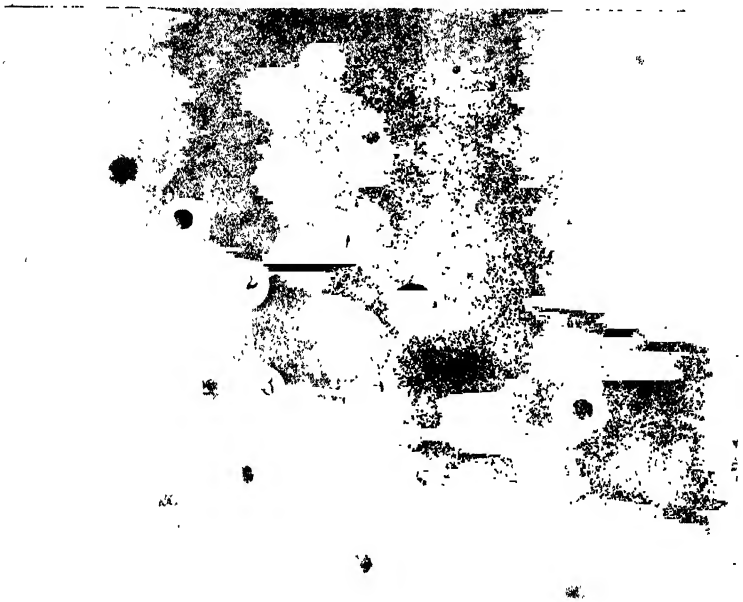


Fig. 2.—Photograph of 3-dimension model representing butylene oxide glucose unit. The numbered black balls represent carbon atoms, those with white circular spots, oxygen atoms, and white balls the hydrogen atoms. The balls are joined by wires representing primary valence bonds; the screw heads visible on the oxygen atoms represent the probable location of secondary valence forces.

formation must occur through the remaining, or first, fourth and fifth positions. Other rings than the 1-4 and 1-5 are, therefore, excluded as possible units in the cellulose structure.

Irvine and Hirst¹² found that the glucose unit in cellulose was a stable, rather than a labile form, and in accordance with conceptions then current, they regarded the unit as having the butylene oxide ring

¹¹ Irvine and Hirst, *J. Chem. Soc.*, **123**, 518-32 (1923).

¹² *Ibid.*, **121**, 1585-91 (1922).

structure. Evidence has since been brought forward by Haworth¹³ and by Hirst¹⁴ to indicate that the normal stable form of glucose, and presumably the form which exists in cellulose, contains not a butylene oxide, but an anylene oxide ring. It will be noted that Irvine's data are equally explainable on the basis of either structure. If the unit contains a 1-5 ring instead of a 1-4 ring as was formerly supposed,

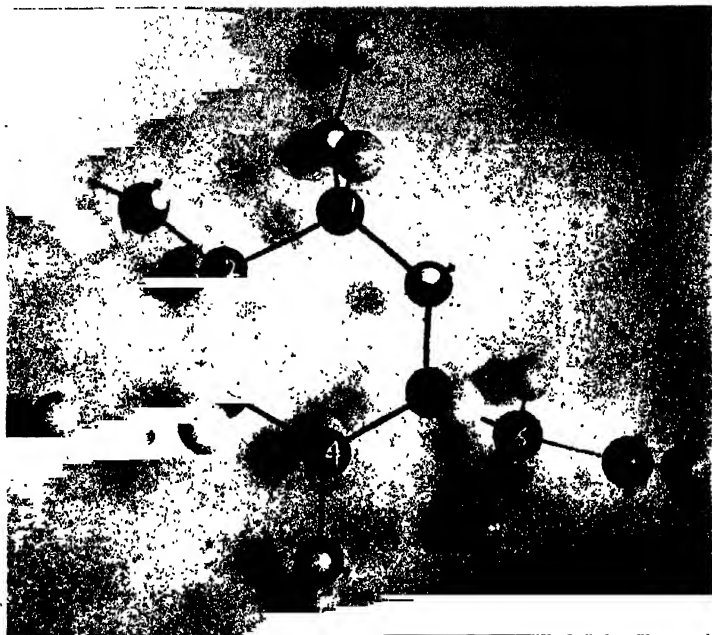


Fig. 3.—Photograph of 3-dimension model representing anylene oxide glucose unit. See explanations under Figure 2.

then the linkage between units would be through the fourth carbon atom instead of through the fifth, but in either case the 2, 3, and 6 positions would remain open for methylation.

In order to obtain a clear conception of the spatial relationships of the constituent atoms of the two glucose structures, and to compare the relative positions of the atoms with the space lattice previously developed for ramie cellulose, it was found desirable to prepare 3-dimension models representing each of these structures. They were carefully

¹³ Charlton, Haworth and Peat, *J. Chem. Soc.*, 129, 89-101 (1926).

¹⁴ *J. Chem. Soc.*, 129, 350-357 (1926).

constructed to a scale based on the atomic radii given by Bragg,¹⁵ care being taken to maintain the tetrahedral angles. Although not representing the modern conception of the nature of the atom, the balls of which the models are constructed serve to indicate rather definitely the relative position of the atomic centers in space. Photographs of these models are shown in Figures 2 and 3 which represent, respectively, the butylene oxide and the amylene oxide structures.

The available chemical data suggest that the continuous chains of atoms indicated by the X-ray data are, in reality, chains of glucose units joined through oxygen bridges to form continuous glucosidal linkages. Since the methylation data indicate through which carbon atoms the linkages occur, it becomes possible to orient the models which represent these units in the lattice derived from ramie fibers, and to compare the dimensions, and the symmetry, of each unit with the requirements developed from the X-ray data.

In Figures 4 and 5 are shown skeleton drawings of the respective units with the hydrogen atoms omitted. The left hand drawings represent the units as they appear in the photographs, while those on the right represent the view at right angles to the photographed positions. The dimension L is assumed to lie in the direction of the fiber length. In the case of the butylene oxide unit, L is the distance between the hydroxyl oxygens on the first and fifth carbon atoms. In the amylene oxide unit, L is the distance between the hydroxyl oxygens on the first and fourth carbon atoms.

Measurements were made of the distance L on both models and the corresponding spacings in Angstrom units were calculated. The following figures were obtained:

For the butylene oxide unit,	27.0 cm. = 5.40 Å. u.
“ “ amylene “ “	25.5 cm. = 5.10 Å. u.
Required by X-ray data	5.15 Å. u.

Since the chains of units are continuous, there are no spaces between units in the longitudinal direction, and there should be a close agreement between the length of the structural unit and the spacing shown by the X-ray data. The length of the amylene oxide unit shows a better agreement with the X-ray data than the butylene oxide unit. Too much significance should not be attached to the mere lack of close agreement in the butylene oxide structure, since it is possible that the actual position of the oxygen atom on the fifth carbon atom may vary from the position assumed for measurement, through rotation or through alteration of one of the tetrahedral angles. However, other positions which might show better agreement with the required length,

¹⁵ *Phil. Mag.*, 40, 169-189 (1920); *Science*, 61, 554 (1925).

would show less favorable agreement with the intensity of certain lines of the X-ray diffraction pattern.

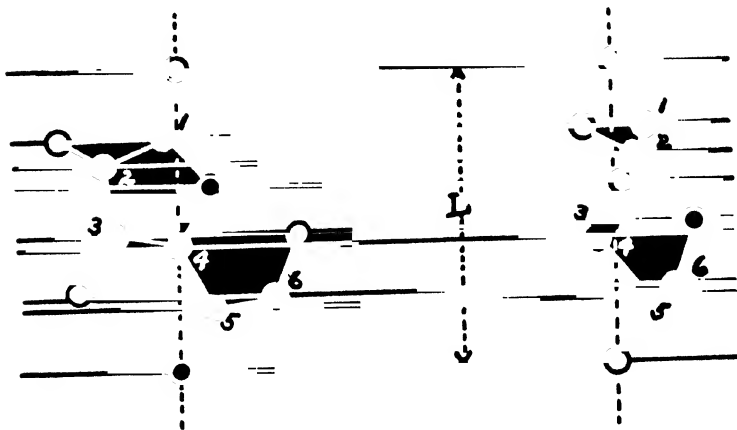


FIG. 4.

Turning now to a consideration of the dimensions at right angles to the length, L , attention must be shifted to the spacing between the chains of units. The X-ray data indicate that there are open spaces

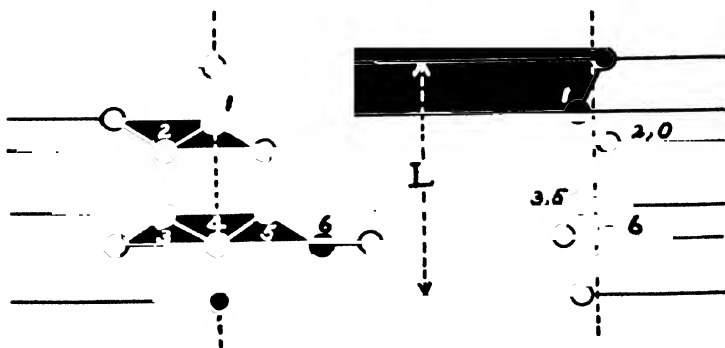


FIG. 5.

between these chains, consequently the dimensions of breadth and thickness would not be expected to show any close relationship to the rectangular spacings, 6.10 and 5.40. Measurements on the models show that either of the units could be accommodated within the spacing, so

again the dimensions fail to indicate definitely which of the two units occurs in the cellulose structure.

On the other hand, considerations of the symmetrical arrangement of the atoms of the two models show that the amylene oxide unit is more in agreement with the X-ray data than the butylene oxide unit. In Figure 5, it will be seen that there is a remarkable balance between the atoms distributed on either side of the vertical axis and that this symmetrical distribution holds for both front and side views. The butylene oxide model, Figure 4, shows a less symmetrical balance in both directions. Of these two forms, the more symmetrical amylene oxide form would be expected to produce a very dense diffraction line especially from the diagonal planes shown in Figure 8, and from the vertical layers of atoms of Figure 9. As will be explained later, these figures represent the arrangement of the units in our completed cellulose structure. For a form like the butylene oxide structure, the unsymmetrical arrangement would tend to place atoms between the layers of Figures 8 and 9, resulting in a much weaker diffraction line for the 3.98 Å. u. spacing. Unfortunately there are no means of making direct comparisons of the intensities referred to, but since the line produced by the 3.98 Å. u. spacing is extremely strong, the evidence favors the amylene oxide structure.

Of much greater significance, however, pointing towards the amylene ring as the probable form, is the arrangement of the atoms on the lines perpendicular to the vertical axis in Figure 5. The regularity of spacing of these horizontal lines agrees well with the type of diffraction pattern produced. [Plate 3, 90° Spectrograph, J. Gen. Physiol. 9, 233 (1925).] On the other hand, it does not seem probable that a structure such as the butylene oxide form in Figure 4 could produce the set of lines which occur on the photograph referred to above. The details of agreement are brought out further on where the transverse planes of the fibers are considered in their relation to the diagrams of the double C₆ unit. (Figures 13, 14 and 15.)

The considerations discussed in the preceding paragraphs seem to justify the conclusion that the amylene oxide ring is the probable form in the cellulose unit.

The amylene oxide unit may have one of two possible forms, depending upon whether the six membered ring has a *cis* or a *trans* structure. A *trans* structure is shown in Figure 5 and a side view of the corresponding *cis* structure in Figure 6. The *cis* form need scarcely be considered for it would throw so many atoms in the space between layers in Figures 8 and 9 that only a faint 3.98 line could be expected, while actually that line is one of the densest produced by the fibers.

The glucose unit may have either an α or β structure. The photograph (Figure 3) shows a β structure, that is, one in which the

hydroxyls upon the first and second carbon atoms are on opposite sides of the ring. Inspection of the 3-dimension model shows that in order to meet the requirement of symmetry and of a continuous straight chain of units, a β structure is necessary. An α structure would produce a *cis* effect at the first carbon and thus fail to fit in the necessary straight

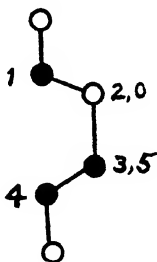
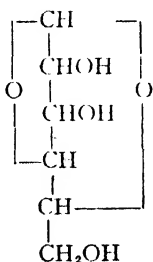


FIG. 6.

chain of units. It is, therefore, assumed that the glucose units of which cellulose is composed are united by β -, rather than by α -linkages.

Before closing the discussion of the selection of a glucose unit, one other possibility demands consideration. Several anhydro-glucose units having two oxidic rings have been proposed as structural units for cellulose, for example the unit:



Units of this type already have an empirical formula $\text{C}_6\text{H}_{10}\text{O}_5$, which indicates that no further dehydration occurs in condensation to cellulose. Such units could not be linked by primary valences, since in that event condensations would be accompanied by the splitting off of water and the formula for the resulting cellulose would contain less hydrogen and oxygen than corresponds to the accepted composition. The units would, therefore, necessarily be joined by secondary valences only. This situation does not agree with certain physical properties which will

be considered further on. Although not definitely excluded as a building unit, this non-continuous structure does not seem a probable one, in the light of the available X-ray evidence. These considerations and, especially the failure of the non-continuous structure to account for the physical properties of cellulose fibers, justify, we believe, the elimination of the double ring structures from this discussion.

Arrangement of the Glucose Units in the Cellulose Structure.

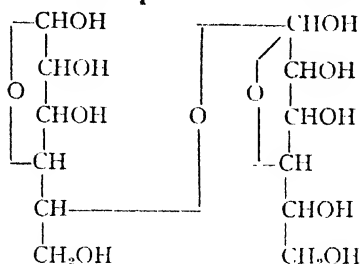
Assuming, then, that cellulose is made up of glucose units possessing amylene oxide rings, our next effort is to determine the arrangement of the building units in the cellulose structure. This resolves itself into two phases, namely: (1) determining the arrangement of the unit in the individual chains, and (2) determining the arrangement of the chains in the cellulose lattice.

Since we have regarded the chains as made up of single ring glucose units in which the condensation has occurred from $C_6H_{12}O_6$ to $C_6H_{10}O_5$, it follows that the union throughout the chain is a continuous series of glucoside-like primary valence linkages. Our next task is, then, to determine the linkage between the glucose units. There are three possible types: (a) one in which C is attached to C_1 and C_1 to C_1 of adjacent units, (b) another in which C_1 is linked to C_4 of the next adjoining unit, and (c) a third in which these two types are combined. In a former paper¹⁰ it was shown that the X-ray data demanded the first type; that is, a reversed orientation of each alternate unit in the direction of the fiber axis, which brings about the 1 to 1 and 4 to 4 linkage. The arrangement of the glucose units is in agreement with the relative intensities of the lines associated with and the spacing of the planes of atoms perpendicular to the long axis of the fiber. It was also shown that the symmetrical type (b) and the combination type (c) would produce different diffraction patterns from those obtained. In other words, the (1-4) (4-1) (1-4) (4-1) linkage satisfied the X-ray data while the other types did not.

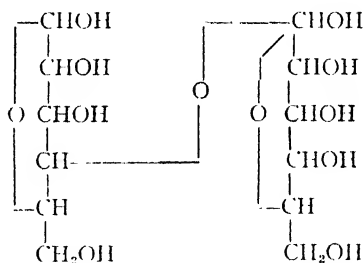
This conclusion is at variance with the commonly accepted belief that cellulose contains cellobiose units. The constitution of cellobiose as derived by Haworth and Hirst¹¹ by means of methylation studies, was that of a glucose-glucoside, the constituent hexose units being united by an oxygen bridge joining the fifth carbon atom of one unit to the first carbon atom of the other:

¹⁰ Sponsler, *J. Gen. physiol.*, **9**, 677-695 (1926).

¹¹ *J. Chem. Soc.*, **119**, 193-201 (1921).



Haworth assumed that the units possessed butylene oxide ring structures, but in view of his more recent work¹⁸ which indicates that the amylenoxide ring is probably the normal structure for glucose, the formula for cellobiose should probably be revised to show a 4-1 linkage between units and should be represented thus:



Since cellulose upon acetolysis yields cellobiose, it has been assumed that cellulose contains units having the cellobiose linkage. If this assumption were correct, the chains of glucose units extending in the direction of the fiber length would necessarily be joined by 1-4 linkages and the X-ray diffraction pattern would be based on C_6 units all oriented alike, whereas the pattern is that of C_{12} units in which the alternate glucose nuclei are reversed.

Although the belief is widespread that cellobiose is a constituent of cellulose, the present authors have been unable to find any convincing evidence in the literature for such a conclusion. In discussing constitutional formulae for polysaccharides, Irvine made the following statement:¹⁹

"In submitting these formulae, it is perhaps necessary to sound a note of caution, as the double assumption is made that maltose is an

¹⁸ Charlton, Haworth and Peat, *J. Chem. Soc.*, 129, 89-101 (1926).

¹⁹ Irvine, *Chem. Reviews*, 1, 62 (1924).

integral part of starch, and similarly that the cellobiose unit is present in cellulose. There seems to be no reason to doubt these conclusions and they are generally accepted, but they have not been proved."

Heuser²⁰ has given a summary of the evidence in support of the claim that "cellobiose preexists in the cellulose molecule" in which it is argued: (1) That since it has been shown that pure cellobiose breaks down under the condition of acetolysis, the yields of cellobiose obtained in practice must necessarily have been smaller than corresponds to the cellobiose-yielding groups actually in the original cellulose. If allowance is made for the losses by secondary reactions, it is estimated that cellulose is capable of yielding 60% or more of cellobiose. It is, therefore, assumed that cellobiose preexists in cellulose to at least that percentage. (2) That the heats of combustion of starch and cellulose, and the nature of their alkali compounds indicate that both are based upon disaccharide units, which are assumed to be, respectively, maltose and cellobiose. (3) That the X-ray of Herzog²¹ and his collaborators are consistent with the cellobiose structure.

Although these observations are not inconsistent with the hypothesis that cellobiose preexists in cellulose, none of them produces evidence which demands the presence of cellobiose units in the original material. Regarding the first argument, it should be noted that the acetolysis reactions are complicated and occur in several stages; and that other explanations for the formation of cellobiose are as acceptable as that based upon direct hydrolysis. Hess and Weltzein²² have advanced the hypothesis that cellobiose is a product formed by the condensation of anhydroglucose units, rather than by a direct hydrolysis of cellulose. Later, Hess, Weltzein and Singer²³ suggested that cellobiose is an intermediate product in cellobiose formation. Since it must be admitted that cellobiose may originate otherwise than by direct hydrolysis of cellulose, evidence bearing upon the yield of product may be dismissed as irrelevant. Regarding the second argument, it need only be said that other disaccharide units than cellobiose would, of course, satisfy the experimental data concerning the heat of combustion and the formation of alkali compounds. As to the third point, the X-ray data of Herzog, which have been taken to indicate the presence of cellobiose units, likewise suggests only the presence of units of C_{12} dimensions, without showing that these units are cellobiose. Sponser's X-ray data also point to a structure based on a double C_6 unit and in addition indicate definitely that the disaccharide units do not possess the cellobiose linkage.

We have now shown that the X-ray data is satisfied by a structure

²⁰ Heuser, West and Esselin, "Textbook of Cellulose Chemistry," 192-3 (1924).

²¹ *Z. Physik*, **3**, 196 (1920); *Cellulosechemie*, **8**, 101 (1921).

²² *Annalen*, **435**, 1-144 (1923).

²³ *Annalen*, **443**, 71-112 (1925).

made up of parallel chains of glucose units which possess an amylenic oxide structure, and which are united by 1-1 and 4-4 linkages. These parallel chains, extending lengthwise of the fiber, are separated from one another by a distance of 6.10 Å. u., from center line to center line, in one direction, and 5.40 Å. u., in the direction at right angles to the 6.10 dimension. Even with these limitations, the chains of atoms would still be free to rotate about their long axes. In the interpretation of the X-ray diffraction patterns, no evidence was advanced from which their orientation might be determined. It now seems possible to make that determination with a considerable degree of definiteness. From measurements on the model, the maximum breadth of the amylenic oxide unit (see Figure 5) is about 7.00 Å. u. Obviously, there is not room for it either on the 6.10 or 5.40 dimension, but it can readily be accommodated on the diagonal of these two dimensions, which has a length of 8.10 Ångstrom units (See Figure 7A). Intermediate positions are, of course, possible between the sides of the rectangle and the diagonal, but reasons will be given for believing that the greatest breadth of the hexose unit lies upon the diagonal.

In accordance with modern conceptions of the nature of valence,²⁴ the oxygen atom is regarded as possessing two primary and two secondary valences tetrahedrally arranged. In the photograph of the amylenic oxide unit (Figure 3), the positions of the secondary valences are shown by small screws. It will be noted that for certain rotation positions of the hydroxyl groups, the forces due to these secondary valences would be exerted along the broadest dimension of the unit. If we assume that these valence forces are attractions, it would follow that the units would tend to become arranged so that the oxygen atoms which exert these forces approach each other as closely as possible. Careful studies with the 3-dimension model show that this condition is realized when all of the units lie with their greatest breadth along the diagonal.

The question arose as to whether the units lie along one diagonal only as in A, Figure 7, or on both diagonals as in B. The second alternative is eliminated by X-ray evidence since that arrangement would produce a different diffraction pattern than is obtained. The pattern would contain not only a line corresponding to the 3.98 spacing of the diagonals, but also one for double that spacing, and that has not been found. We have adopted, therefore, the arrangement as shown in Figure 7, A.

In the alternate diagonal planes the positions of the units are reversed; that is, the chains are rotated through 180° about an axis parallel to the fiber length. That arrangement was demanded by the presence of certain lines on the diffraction patterns taken when the

²⁴ See G. N. Lewis, "Valence and the Structure of Atoms and Molecules" (1923).

X-ray beam made other angles than 0° or 90° with the fiber axis; these lines demanded a different arrangement of the atoms in adjacent groups. If the chain of groups had the same orientation, such lines as the 4.35, 3.25 and 3.10 of the (111) series would not occur. This point is brought out in more detail in the earlier paper.²⁵

As a result of this line of reasoning, a structure has been developed for ramie cellulose which is apparently consistent with all of the X-ray data and with the established facts of cellulose chemistry. This structure is shown in the accompanying photographs of the model (Figures 8, 9, 10, 11 and 12). The model contains four chains, each containing two glucose units, making eight glucose units in all. In Figure 8, the model is viewed along the fiber axis and shows the distribution of the

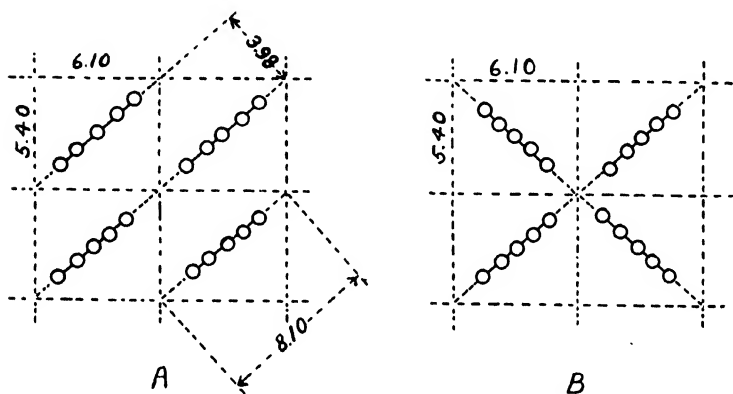


FIG. 7.

four chains upon the 6.10 x 5.40 spacing. The units are shown as lying upon the diagonal and the planes formed by them correspond to those with the 3.98 Å. u. spacing. Actually, the open spaces between the units are smaller than appear in the photograph, since almost all of the hydrogen atoms occur in these spaces. The hydrogen atoms were not represented on the model because they do not appreciably enter into the production of the X-ray diffraction patterns. Figure 9 shows the same groups viewed along the diagonal planes. The open spaces are again apparent and the reversed arrangement of the units on the alternate diagonals may be seen here. Figure 10 shows the model viewed along the 5.40 dimension perpendicular to the fiber length; Figure 11 is also viewed perpendicular to the fiber axis, but along the other diagonal of the 6.10 x 5.40 rectangle.

²⁵ Sponsler, *J. Gen. Physiol.*, 9, 677-695 (1926).

The eight glucose residues shown in the model constitute the simplest structure in which all orientations of the C_6 groups occur. In the strictest sense, they would constitute only one-fourth of the whole crystallographic unit, the axial ratios of which would be $a : b : c = 10.80 : 12.20 : 10.25$. Figure 8 is a view along the c axis. Figures 10 and 12 are views along the a and b axes, respectively, but represent only



FIG. 8.—Photograph of 3-dimension model representing the structure of ramie cellulose, viewed along the fiber axis. Four of the double C_6 units are shown. Black balls represent carbon atoms, white balls, oxygen atoms. Hydrogen atoms are omitted but their positions are indicated by the short pointed wires. The screw eyes represent the probable location of the secondary valence forces.

half the length of those axes. In Figures 9 and 11, the structure is seen along the $(\bar{1}10)$ and (110) planes, respectively.

While it was found possible to further test the agreement between the model and the X-ray data, it does not seem probable that a complete accounting can be made of all the diffraction lines. Therefore, we have had to content ourselves with a study in which only a few of the more prominent lines were considered, which seem to have been produced by the simpler planes of this complex structure; and have accepted the agreement as being good if the model showed a relatively large num-



FIG. 9.—Photograph of 3-dimension model representing the structure of ramie cellulose, viewed along one of the diagonal planes perpendicular to the fiber axis. See explanations under Figure 8.

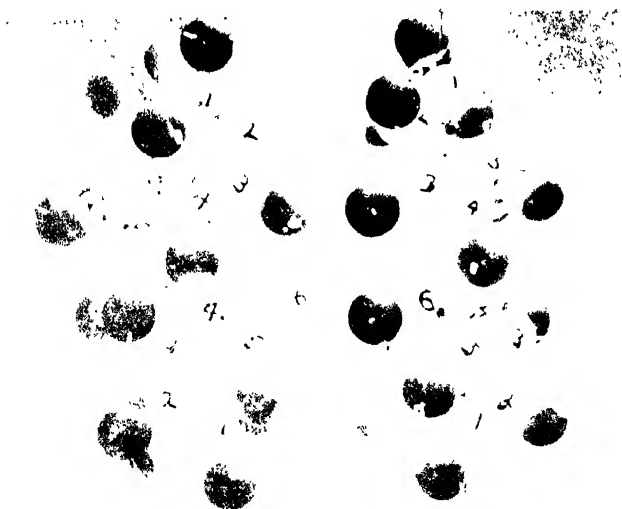


FIG. 10.—Photograph of 3-dimension model representing the structure of ramie cellulose, viewed along the 5.40 dimension perpendicular to the fiber axis. See explanations under Figure 8.

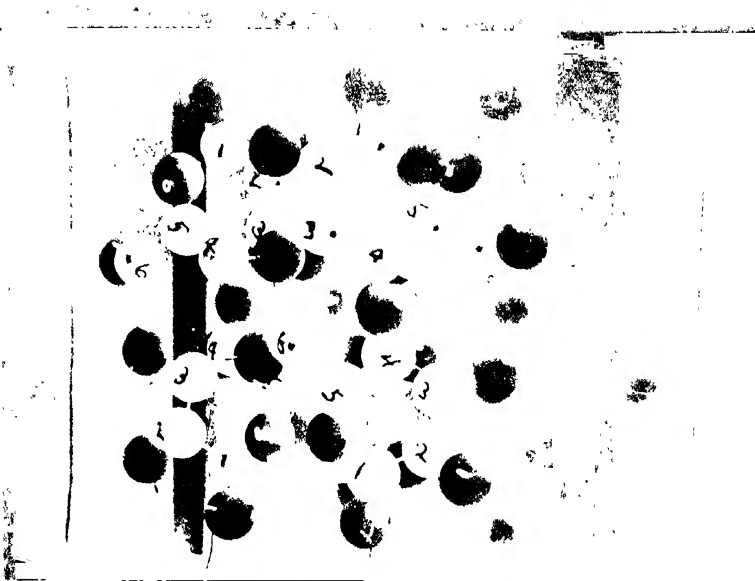


FIG. 11.—Photograph of 3-dimension model representing the structure of ramie cellulose, viewed along one of the diagonal planes perpendicular to the fiber axis. See explanations under Figure 8.



FIG. 12.—Photograph of 3-dimension model representing the structure of ramie cellulose, viewed along the 6.10 dimension perpendicular to the fiber axis. See explanations under Figure 8.

ber of atoms occurring in layers at angles which agreed with the observed lines and the observed angles. The interplanar spacings of the transverse planes, those which form a 90° angle with the fiber axis, are pictured in Figures 13, 14 and 15, where only the carbon and oxygen atoms are indicated. By using a graphic method for deter-

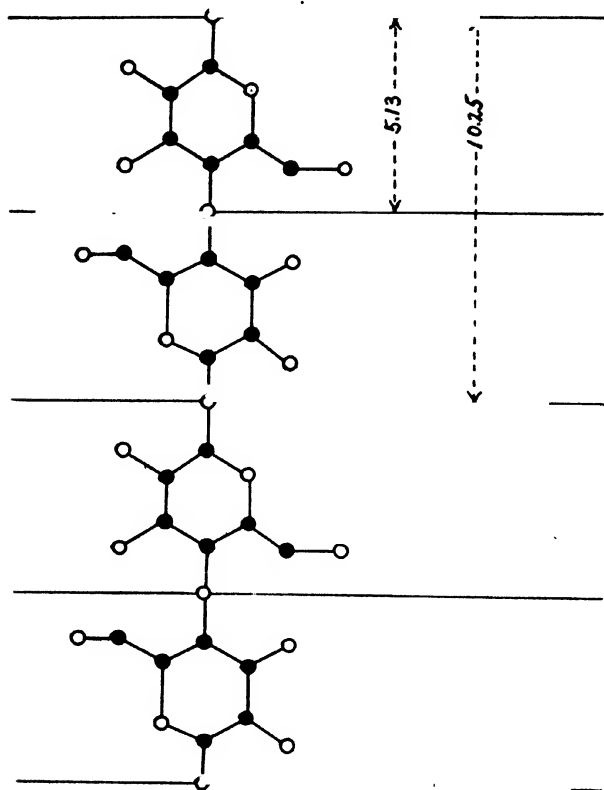


FIG. 13.—Diagram showing part of a chain of glucose units with hydrogen atoms omitted and indicating the relation of the 5.13 and 10.25 transverse planes.

mining the resultant amplitudes of the reflections, the intensities of the corresponding diffraction lines were obtained. The agreement between the calculated and actual intensities was fairly good, in this sense at least, that the 2.58 line was denser than the 1.70, and that both were much denser than the 3.40 and the 5.15 lines. On account of the reversed orientation of the C_6 units and of the chains on their long axis,

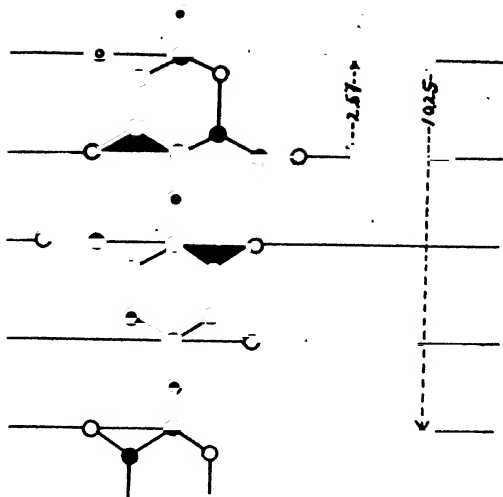


FIG. 14.—Similar to Figure 13, indicating relation of the 2.57 and 10.25 transverse planes.

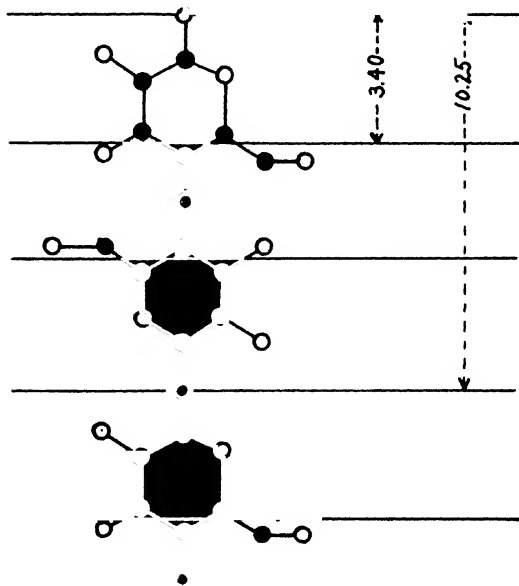


FIG. 15.—Similar to Figures 13 and 14, indicating relation of the 3.40 and 10.25 transverse planes.

it seems almost impossible to check the diagonal planes against the intensities of the diffraction lines produced by them.

From Figure 8 and its simpler diagrammatic representation in Figure 7A, one can see that the 3.98 diagonals would produce a much more intense line than either the 5.40 or the 6.10 planes; and that they in turn would produce lines of much more nearly equal intensity, agreeing qualitatively with the diffraction pattern for these planes. No models have been constructed yet which would make a quantitative comparison seem feasible.

Relation of the Structure to the Physical Properties of Ramie Cellulose.

As was pointed out in Sponsler's first paper,²⁶ ramie fibers are cylindrical tubes whose walls are made up of concentric shells of cellulosic material. It is consistent with the X-ray data to assume that

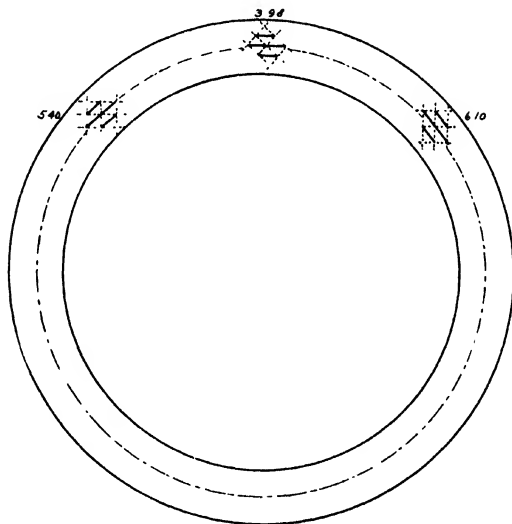


FIG. 16.—Diagram of cross-section of ramie fiber showing location of elementary cell in fiber wall.

the 6.10 x 5.40 rectangular spacings are distributed throughout the cell walls in the positions that would result if the crystallographic units were rotated about the central axis of the cylinder as a line of symmetry. Some dimension of the 6.10 x 5.40 rectangle would have a

* Sponsler, *J. Gen. Physiol.*, 9, 221-233 (1925).

constant tangential position in the cylindrical shell. Uncertainty was then expressed as to which dimension had the tangential position. It now appears most consistent with the facts to assume that it is the 3.98 diagonal which occupies that position, the units on that dimension being held together in a more or less complete cylindrical shell by the secondary valences. It is also consistent with our knowledge of plant physiology to regard these concentric layers as successively deposited from within by the protoplasm of the cell. The relationships mentioned here are shown in Figure 16.

Having developed this conception of the structure of the ramie fiber, it becomes possible to account for the stability of this and similar cellulosic fibers, as well as for some of their characteristic physical properties. The stabilizing forces in the fibrous structure are assumed to be the valence forces. The primary valence linkages in the longitudinal direction establish the chemical and mechanical stability of the long chains. The positions of these chains with respect to each other are stabilized by the attractions of secondary valence on the potentially quadrivalent oxygen atoms. These forces tend to draw the chains together; complete contact is opposed by the external hydrogen atoms which resist invasion of their atomic domains. Equilibrium between these opposing forces fixes the relative positions of the chains upon the corners of the 6.10×5.40 rectangle. The relationships are shown in Figures 17 and 18 which represent, respectively, tangential and radial sections of the fiber wall.

This structure explains the great tensile strength of the fibers in the longitudinal direction, since in order to break them, it is necessary to rupture the primary valence bonds (indicated by solid lines in the figures) that hold the hexose units together. On the other hand, it is well known that the fibers possess comparatively little strength in directions at right angles to the fiber length. This also is explained by the proposed structure, since a separation of the chains in a radial or a tangential direction would be a matter of overcoming the weaker forces of the secondary valence attractions, the general direction of which is indicated by the broken lines.

Hendershot²⁷ has presented data to show that the coefficient of thermal expansion of wood is approximately ten times greater in the direction at right angles to the grain than in the direction parallel to the grain. Thermal expansion is associated with molecular agitation and should be greatest when the freedom of movement is greatest. In our proposed structure, a smaller coefficient of expansion would be expected in the direction of the fiber axis than in the direction at right angles to it. The expected behavior is, therefore, in agreement with Hendershot's findings.

²⁷ *Science*, **60**, 456 (1924).

The swelling of fibers by the absorption of water may also be accounted for by this structure. It is well known that cellulosic fibers in general show little or no swelling in the longitudinal direction, but swell considerably in the lateral direction. Since the linkages in the

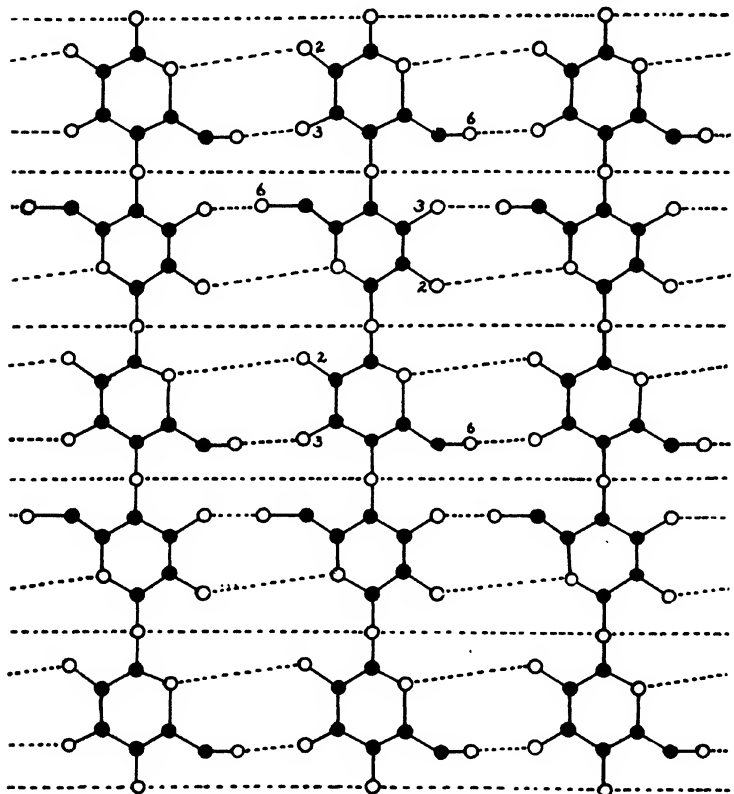


Fig. 17.—Tangential section through a ramie fiber showing three chains of glucose units. Dark lines indicate primary valence bonds; broken lines indicate probable general direction of secondary valence forces.

direction of the fiber length are by primary valences, there is no opportunity for water molecules to enter between the units, and no longitudinal swelling can occur. On the other hand, water molecules can be adsorbed on the oxygens by the action of secondary valence forces. The spacing between the chains of units, then, necessarily becomes

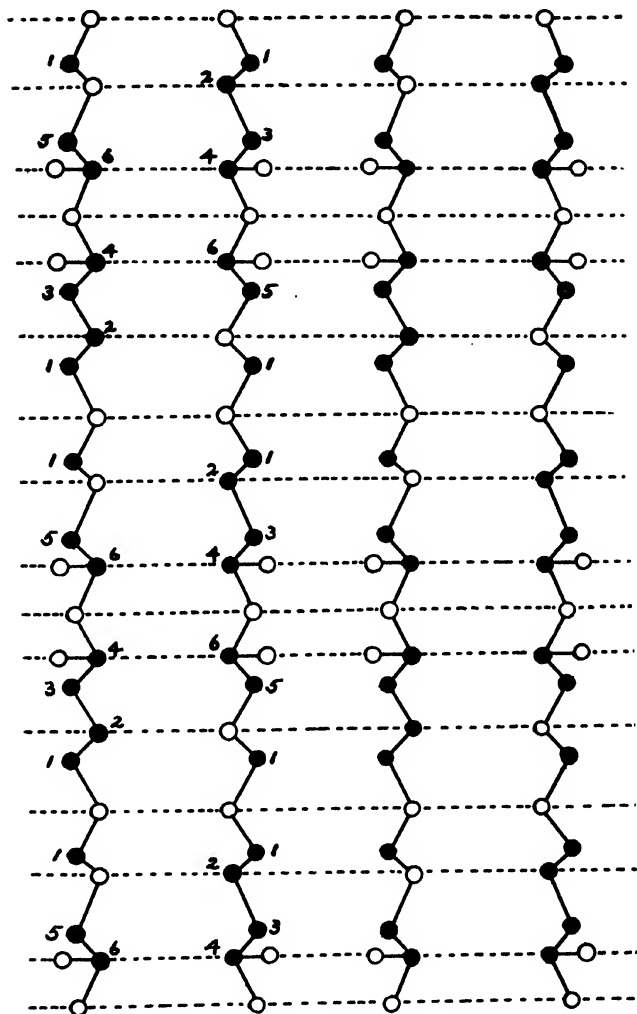


FIG. 18.—Radial section through a ramie fiber. See explanations under Figure 17.

wider in order to accommodate the water molecules, and lateral swelling occurs. In this connection, some direct data are available. Katz²⁸ found by X-ray methods that a shift occurred in the position of the

²⁸ *Phys. Z.*, 25, 321-326 (1924).

diffraction points when certain fibers were swollen. Unpublished data by Sponsler on hemp fibers show that the planes spaced 2.58 Å. u. retained that spacing in both wet and dry fibers, while the spacing of 3.98 Å. u. became greater by about 2 per cent in the wet fibers. This would correspond to a change in the radial dimension of the fibers on swelling, while the longitudinal dimensions remained unaltered.

Relation of the Structure to the Chemical Properties of Ramie Cellulose.

The formation of the various cellulose esters occurs by replacement of the three hydroxyl groups that are open for substitution. These are shown in the photographs of the model and in the drawings, especially in Figure 17 where they are represented by numbered circles. In some cases of ester formation, the fibrous structure is maintained and it is clear from the illustrations that replacement of the hydroxyls might readily occur without disturbing the general fibrous structure since a separation of the longitudinal chains to accommodate the replacing groups would be all that is necessary. This agrees with statements by Denham and Woodhouse²⁹ and by Irvine and Hirst,³⁰ that methylated cellulose retains the fibrous form of the original cellulose.

The structure was developed upon the assumption of the correctness of Irvine's conclusion, that when cellulose is methylated, replacement of hydroxyl groups occurs on the second, third and sixth carbon atoms; and reference to the figures will show that these carbon atoms and no other carry hydroxyl groups open for substitution. It should be pointed out, however, that the conclusion to which we have just referred has not gone unchallenged. Hess³¹ has expressed the belief that cellulose is modified by treatment with alkaline solutions, of the strength used in methylation, possibly causing a change in the positions open to substitution; consequently conclusions as to the structure of cellulose based upon the ascertained structure of its methylated product may not be valid.

Alterations of the type referred to by Hess can be shown to be rather improbable when we interpret, in terms of our proposed structure, some recent X-ray investigations by Katz and Mark³² on the swelling of cellulose fibers in alkaline solution. The data obtained by these authors indicate that there is some alteration in structure upon adding alkali, but that on washing out the alkali, the original structure reappears, differing only by slight enlargement of some of the dimensions. Some of Herzog's most recent data³³ give similar in-

²⁹ *J. Chem. Soc.*, **103**, 1795 (1913); **119**, 77 (1921).

³⁰ *J. Chem. Soc.*, **123**, 518-92 (1923).

³¹ Hess and Weltzien, *Liebigs Ann.*, **435**, 1-144 (1923).

³² *Z. physik. Chem.*, **115**, 885-904 (1925).

³³ Herzog, *J. phys. Chem.*, **30**, 455-67 (1926).

dications. This behavior, like simple swelling with water, is explainable on the assumption that alkali molecules enter between the longitudinal chains and so cause lateral expansion. The alterations are consequently changes in the relative positions of the longitudinal chains, and not changes within the chains themselves. It is conceivable that it is the action of the alkali in forcing apart the longitudinal chains that makes possible the entrance of the methoxyl groups during the methylation reaction. At any rate, it is consistent with the proposed cellulose structure, as well as with the observed facts, to assume that treatment with alkalis and methylating agents produces a methylated cellulose which is still fibrous, and which differs from the original cellulose structure only in the greater separation of the longitudinal chains.

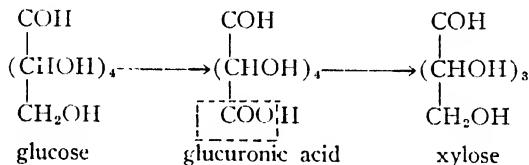
Although replacement of the side hydroxyls should not affect the integrity of the longitudinal chains, the increased separation of the chains by substitution of larger groups for the hydroxyls would tend to weaken the fibrous structure, and it is conceivable that very large groups might so far separate the longitudinal chains as to render ineffectual the lateral stabilizing forces. The fibrous structure would then tend to become destroyed, by the bending or collapsing of the long chains. This condition may explain the fact that cellulose nitrates retain the fibrous structure much better than do the corresponding cellulose acetates. In order to accommodate the acetate groups, a wider separation of the chains is required than for the nitrate groups, and possibly the distance may be so great, in the case of the acetate groups, that the lateral forces are no longer able to maintain the relative positions of the chains as they existed in the unsubstituted cellulose.

Consistent with our postulated structure, we may assume that the breakdown of the fibrous structure of cellulose, under the action of various chemical treatments, begins with the separation of the longitudinal chains. Depending upon the nature of the treatment, subsequent solution and hydrolysis of the separated chains may occur; for example, in simple acetylation, proceeding only as far as the production of the triacetate, the longitudinal chains may remain intact, while in the case of acetolysis in which a higher degree of acetylation is attained, the chains are split up into units of C_{12} or C_6 dimensions. Once the fibrous structure is lost, the possibilities for rearrangement are almost infinite. Apparently no evidence is yet available to indicate what types of structure may occur in the stages immediately succeeding the breakdown of the fibrous structure.

So far there is no complete evidence that the structure which we propose for ramie cellulose applies to other naturally occurring celluloses, such as cotton, wood, esparto, etc. Nevertheless, the fact that the structure explains so many of the general properties and re-

actions of cellulose fibers would suggest that it represents, possibly with modifications, the general structure of all fibrous cellulosic material.

In some types of cellulose, for example, the cellulose derived from wood, or from esparto, xylose units are invariably found associated with the hexose units which make up the cellulose structure. The presence of these pentose units may be explained on the assumption that these types of cellulose possess structures similar to that which we have postulated for ramie cellulose. Hibbert and Parsons³⁴ have shown that in the oxidation of cellulose (to so-called oxylcellulose), the primary alcohol group, or the group involving the sixth carbon atom, becomes oxidized first to an aldehyde group and finally to a carboxyl, thus producing a glucuronic acid unit. It is known that sugar acids of this type readily undergo decarboxylation with the formation of pentoses; in the case of glucuronic acid, the corresponding pentose is xylose. Since the normal form of xylose, like that of glucose, is now regarded as having the amylene oxide structure,³⁵ we may logically regard the xylose units as produced in such structures as we have proposed by successive oxidation and decarboxylation of some of the glucose units according to the scheme:



It was suggested some years ago by Spoehr³⁶ that the formation of pentoses in plants might occur by reactions of this type. The important observation in connection with the present conception of cellulose structure is that this type of reaction can readily occur without disturbing the fibrous structure; this is in accord with the fact that celluloses which contain xylose possess the same fibrous structure as the celluloses which are made up wholly of hexose units.

The researches of Irvine and Hirst³⁷ on esparto cellulose and of Heuser and Haug³⁸ on straw cellulose appear to indicate that the xylose portions of these celluloses are localized in alkali soluble xylan units, rather than that pentose and hexose units exist in intimate union distributed throughout all parts of the fiber. This would suggest, in terms of our postulated structure (see Figure 17) that in certain chains, all of the glucose units had become converted into xylose units by the

³⁴ *J. Soc. Chem. Ind.*, **44**, 473T-485T (1925).

³⁵ Haworth, *Nature*, **116**, 430 (1925).

³⁶ Carnegie Inst. Publication No. 287, p. 78.

³⁷ *J. Chem. Soc.*, **125**, 15-25 (1924).

³⁸ *Z. angew. Chem.*, **31**, 99-100, 103-4 (1918).

described processes of oxidation and decarboxylation, and that these altered chains constitute the xylan units. Consistent with the views of Netthöfel,³⁹ the altered portion of the fiber would be the exposed inner and outer surfaces of the cylindrical tube that constitutes the fiber.

The present authors do not wish to go further than to point out that there is a remarkable agreement between the proposed structure for ramie cellulose and the known properties and behavior of cellulose fibers. Many of the suggested relations that have been mentioned in this paper are capable of, and indeed require experimental confirmation. It is our intention, as opportunity permits, to carry out experimental studies to further clarify the nature of cellulosic fibers.

Summary.

1. A conception of the structure of ramie cellulose is described, based on previously published X-ray data and upon studies with stereochemical models. The proposed structure agrees with the space lattice indicated by the X-ray data and is apparently consistent with all of the physical properties and chemical reactions of fibrous cellulose.

2. The cellulose structure is made up of glucose units. Of the various possible structural formulae for glucose, it is shown that the amylose oxide ring formula is in closest agreement with the X-ray requirements. It is accordingly accepted as the probable structural unit of cellulose.

3. The glucose units are apparently united in chains of indefinite length by glucosidal condensation. The union between units is alternately a 1-1 and a 4-4 linkage. The X-ray data indicate that the 1-4 linkages, characteristic of cellobiose, do not exist in the ramie cellulose structure.

4. The chains of glucose units are spaced rectangularly 6.10×5.40 Angstrom units apart. The greatest breadth of the glucose units lie along one of the diagonals of the 6.10×5.40 rectangle.

5. A group of eight glucose units is the simplest unit that can represent the structure of cellulose. This corresponds to the crystallographic unit with axes: $a = 10.80$; $b = 12.20$; and $c = 10.25$ Angstrom units.

6. The ramie fiber is a hollow cylinder, in the walls of which the crystallographic units are distributed so that one of the diagonals of the 6.10×5.40 spacing always occupies a tangential position.

7. The cellulose structure is stabilized longitudinally by the primary valence forces that unite the glucose units; it is stabilized laterally by the secondary valence forces of the oxygen atoms.

³⁹ See Heuser, West and Esselin, "Textbook of Cellulose Chemistry," 123 (1924).

8. The proposed structure accounts for the tensile strength of the fibers in the longitudinal direction. It also explains the different longitudinal and lateral thermal expansions, and accounts for swelling phenomena.

9. The structure is in agreement with Irvine's methylation data in that the hydroxyls upon carbon atoms 2, 3, and 6 are open for substitution. Ester formation is shown to be possible without alteration of the fibrous structure other than separation of the longitudinal chains. This, however, may weaken the fibrous structure and if the introduced groups are large, the secondary valence forces may become unable to stabilize the fibrous arrangement.

10. Since the structure for ramie cellulose agrees with the nature of cellulose fibers in general, it appears likely that other celluloses possess a similar structure.

11. The presence of xylose units in some celluloses may be accounted for by assuming that oxidation of glucose units to glucuronic acid occurs with subsequent decarboxylation to xylose. In the proposed structure, these changes would not materially alter the original fibrous structure.

University of California.

ORGANOPHILIC COLLOIDS

BY G. STAFFORD WHITBY

In the early period of colloid chemistry attention was directed largely to inorganic substances in the colloid state and especially to lyophobic systems such as sols of gold, silver, arsenic sulfide, etc. Later lyophilic systems, so much more important both physiologically and industrially than lyophobic ones, became the main object of study. The lyophilic colloids studied have, however, until very recently, been almost exclusively hydrophilic. But it is not difficult to observe a tendency among colloid chemists to bestow an increasing measure of attention on that class of lyophilic colloids which swells in and form sols and gels with, not water, but organic liquids—the organophilic colloids.

It is not to be denied that among lyophilic colloids the hydrophilic ones are of supreme importance because of their intimate relation to the processes of life. The behavior of the hydrophilic colloids is, however, complicated by the circumstance that, on account of the presence of water, they are much subject to ionic and electrical influences. And the proteins are subject to an additional complication, in that they are amphoteric. The organophilic colloids, by contrast, would appear to be little subject to such complications, since the media in which they form sols and gels are usually non-ionizing. It would not be unfair to say that in organophilic colloid systems the *essential* features of colloids are presented without the complicating accessory features found in the case of hydrophilic colloid systems. This consideration affords sufficient general justification for urging the value in the development of the theory of lyophilic colloids of a fuller study of the organophilic colloids than has hitherto been made. The object of the present paper is not to attempt any exhaustive or systematic survey of our present knowledge of the organophilic colloids, but merely to offer some notes on certain of the points concerning this class of colloids which appeal to the writer as being of interest and deserving of further study.

It may further be remarked that the organophilic colloids are deserving of fuller study, not only because of the contributions which such study can make to the development of colloid theory, but also because a not inconsiderable number of them are of great industrial

importance. In this connection it is interesting to note that, whereas most of the hydrophilic colloids are natural products, most of the organophilic colloids are artificial products. I need but recall the proteins, starch, pectin, saponins, agar, gums on the one hand; vulcanized rubber, nitrocellulose, acetocellulose, linnoxyn on the other.¹ This state of affairs is what might have been expected from the fact that life first developed in water and that the processes of life take place in aqueous, not organic, media.

In view of the fact that the organophilic colloids are mostly artificial products, it may safely be asserted that, with the progress of discovery, their number will greatly increase in the future.

Relation Between the Chemical Character of the Organophilic Colloids and That of the Liquids Which They Imbibe.

Since the medium in which a purely hydrophilic colloid disperses is always water, whereas an organophilic colloid is dispersable in many different media, a problem presents itself at the outset in connection with the organophilic colloids which does not arise in connection with the hydrophilic: the problem, namely, of the relation if any between the chemical structure of the colloid and that of the media in which it is dispersable. Undoubtedly the chemical structure of liquids determines their ability first to bring about first swelling and then dispersion of a given organophilic colloid, as the following data will show.

Rubber and Cellulose Esters:

In the course of measurements of the swelling of rubber, both raw and vulcanized, in more than 350 organic liquids, which have been carried out in the author's laboratory during the past three years and a full account of which will be published shortly, many regularities have been observed in regard to the relation between the chemical structure of liquids and their imbibition by rubber. It has been found that, in addition to the recognized solvents for rubber, *i.e.*, hydrocarbons and chlorinated hydrocarbons, liquids belonging to many other classes are capable of swelling raw and vulcanized rubber and of dispersing the former. In general it has been found that in any homologous series of compounds containing an active group, such as a hydroxyl, nitrile, aldehyde, or carbonyl group, imbibition by rubber

¹ Raw rubber might perhaps be urged as an exception to this generalization. But it is at all events to be noted that in nature rubber occurs in a lyophobic system. The rubber hydrocarbon does not swell in water. In nature it occurs in an aqueous medium as unswollen globules maintained in suspension by means of a protective colloid—protein. Its organophilic properties play, so far as we know, little part in nature. Only in the industrial arts does it function as an organophilic colloid.

A real exception to the generalization stated in the text is probably to be seen in phytoosterolin, to which a paragraph is devoted later.

increases as the series is ascended. This is exactly the reverse of the case with nitro- and aceto-cellulose.²

And no better method of emphasizing the relation between the chemical character of an organophilic colloid and that of the media in which it swells and may be dispersed can, I believe, be followed than to institute a comparison between the solvents for rubber on the one hand and for cellulose nitrate and acetate on the other.

With a certain limited number of exceptions, solvents for the common cellulose esters are non-solvents for rubber, and, conversely, solvents for rubber are non-solvents for the cellulose esters. Speaking very broadly, the case may perhaps be stated thus: cellulose nitrate and acetate, representing a trihydric compound esterified with respectively an inorganic acid and a fatty acid of low molecular weight, are polar substances and in general imbibe and yield sols with polar organic liquids, *i.e.*, with the lowest members of organic series containing active groups, while rubber, a hydrocarbon, is non-polar and in general imbibes most freely and when unvulcanized yields sols with liquids of low polarity, *i.e.*, with hydrocarbons, halogenated hydrocarbons, and the higher members of series containing active groups. In general, compounds containing active groups are swelling agents for rubber only if they contain as well hydrocarbon residues of some length; and, the larger the hydrocarbon residue, the greater is the extent to which they are imbibed. Conversely, long hydrocarbon residues are unfavorable and active groups favorable to the dispersion of cellulose esters. Compounds containing active groups are solvents for the cellulose esters only if the hydrocarbon residues present are small. Consider the behavior of rubber and of cellulose acetate to a number of types of compounds.

Hydrocarbons, etc. Hydrocarbons are in general good swelling agents for rubber and non-solvents for the cellulose esters. For example: petroleic ether is a non-solvent for cellulose esters,³ and turpentine does not dissolve cellulose acetate.⁴ It is interesting to note that the sesquiterpene, caryophyllene, which was the only exception encountered to the general rule that hydrocarbons are good solvents for rubber, will dissolve cellulose acetate and yield gels with it.⁵

The stereoisomeric sym.-dichlorethylenes present an interesting case. Walden and Werner⁶ found these isomers to differ noticeably in dielectric constant, the *cis*- compound having a dielectric constant about half that of the *trans*- compound. Our measurements showed that the *cis*- compound has a higher swelling power for rubber than

² Vide Mardles, *J. Soc. Chem. Ind.*, 42 128T (1923); McBain, Harvey and Smith, *J. phys. Chem.* 30, 335 (1926).

³ Cf. *e.g.*, Sproxtton, *Third Rep. Colloid Chem.*, p. 84.

⁴ Fenton and Berry, *Proc. Camb. Phil. Soc.*, 20, 16 (1920).

⁵ Data for which no literature references are given are from the author's laboratory.

⁶ *Z. physik. Chem.*, 111, 465 (1924).

the trans- isomer, and, in accord with this finding, that it is a better precipitant for cellulose acetate. 10 ccs. of a 2.5 per cent solution of cellulose acetate in acetone required about 14 ccs. of the cis- and about 24 ccs. of the trans- compound to produce turbidity. That is to say: the isomer which swells rubber the more is the more effective in de-solvating cellulose acetate.

Aldehydes. Acetaldehyde, in which an active group is attached to a short hydrocarbon residue, is a solvent for cellulose acetate,⁷ and a non-solvent for rubber. If the hydrocarbon residue attached to the same active group is lengthened, the position gradually becomes reversed: solvent action on cellulose acetate falls off and imbibition by rubber increases. Thus heptaldehyde fails to dissolve cellulose acetate,⁸ but dissolves raw rubber. Salicylaldehyde,⁹ anisaldehyde, and cinnamyl aldehyde all dissolve cellulose acetate, but are very poor swelling agents for rubber.

Ketones. Acetone is a very good solvent for the ordinary cellulose acetate; it will precipitate rubber from solution. Methyl ethyl ketone is a poorer solvent for cellulose acetate than is acetone,¹⁰ but the position is reversed in regard to the swelling of rubber: methyl ethyl ketone produces a little swelling, whereas acetone produces none at all, and, in accord with this, very much more methyl ethyl ketone than acetone is required to precipitate rubber from a given solution. It is necessary to go only to the next member of the series, viz. diethyl ketone to encounter a liquid which will not dissolve cellulose acetate but will dissolve rubber. The next member, ethyl propyl ketone, is, similarly, a solvent for rubber and a non-solvent for the acetate.

The initial product of the acetylation of cellulose is soluble in chloroform and almost insoluble in acetone. In the industrial production of cellulose acetate, the initial product is usually treated with water according to the Miles process. This treatment if carried far enough renders the acetate soluble in acetone and insoluble in chloroform.¹¹ This state of affairs is in accord with the point of view here under consideration. The partial hydrolysis which the treatment produces would, by increasing the polar character of the cellulose acetate, increase its affinity for a polar molecule such as that of acetone and diminish its affinity for a non-polar substance such as chloroform.

Nitro compounds. Another active group, the presence of which usually results in a high dielectric constant and favors solution of cellulose acetate but which is unfavorable to the swelling of rubber, is the nitro group. Nitrobenzene has long been known as a solvent for

⁷ Fenton and Berry, *loc. cit.*

⁸ Mardles, *J. Soc. Chem. Ind.*, 42, 127T (1923).

⁹ Fenton and Berry, *loc. cit.*

¹⁰ Mardles, *loc. cit.*

¹¹ Cf. e.g., Worden, "Technology of the cellulose esters," 1916, vol. 8, 2574.

cellulose nitrate; it is also a solvent for the acetate.¹² It does not dissolve rubber, and is a comparatively poor swelling agent for that material. Nitromethane is not imbibed by rubber, but is, I find, a very good solvent for cellulose acetate, taking up large quantities in the cold. While the ether anisole is a good rubber solvent and a non-solvent for cellulose acetate, the introduction of a nitro group, as in o-nitranisole, destroys the ability to swell rubber, but confers solvent power for cellulose acetate.

Nitriles. Acetonitrile, a liquid with a high dielectric constant, dissolves cellulose acetate,¹³ but entirely fails to swell rubber. If, however, as in capronitrile, $C_5H_{11}CN$, the hydrocarbon residue is increased considerably in size, a nitrile produces some swelling of rubber and is only a very poor solvent for cellulose acetate. (Capronitrile will dissolve cellulose acetate on boiling, but the latter separates again on cooling.) Phenylacetonitrile produces hardly any swelling of rubber; it will dissolve cellulose acetate.

Anhydrides. Acetic anhydride is well known to dissolve cellulose acetate; it swells rubber hardly at all. If, however, the homologous series is ascended to the n-valeric compound, $(C_4H_9CO)_2O$, it is found that the anhydride swells rubber but is a very poor solvent for cellulose acetate. (The acetate will dissolve in boiling valeric anhydride, but separates on cooling as a gelatinous precipitate.)

Hydroxy compounds. The presence of the hydroxyl group, particularly in the aliphatic series, by rendering the molecules polar, tends to produce solvent power for cellulose acetate and lack of such power for rubber. Only if a long hydrocarbon chain is attached to the hydroxyl group are in general hydroxy compounds imbibed by rubber, and even then only to such a small extent that they will not disperse the rubber. The lower alcohols will dissolve cellulose acetate on heating, but the solvent power falls off from methyl to ethyl to butyl alcohol.¹⁴ Rubber has such little affinity for methyl and ethyl alcohols that these liquids will precipitate it from solution. As the series is ascended, however, alcohols lose the ability to precipitate rubber; they acquire ability to swell rubber and lose ability to dissolve cellulose acetate. Heptyl alcohol will dissolve cellulose acetate only on boiling, and the acetate separates on cooling, while octyl alcohol will not dissolve cellulose acetate even on boiling, but will produce some swelling of rubber.

Ethylene chlorhydrin,¹⁵ monochlorhydrin, and dichlorhydrin are solvents for cellulose acetate. They produce practically no swelling of rubber. If, however, the hydroxyl groups are completely replaced

¹² Fenton and Berry, *loc. cit.*

¹³ *Ibid.*

¹⁴ Mardles, *loc. cit.*

¹⁵ Putman and Kirst, U. S. Pat., Feb. 14, 1922.

by chlorine, as in ethylene dichloride and trichlorhydrin, good solvents for rubber at once appear.

Other hydroxy compounds which are solvents for cellulose acetate but produce little or no swelling of rubber are: benzyl alcohol,¹⁶ phenol, cresol,¹⁷ cyclohexanol, diacetone alcohol, the monomethyl ether of ethylene glycol,¹⁸ eugenol,¹⁶ lactic acid,¹⁹ ethyl lactate. Under the head of hydroxy compounds reference may be made to thioglycollic acid. This swells rubber hardly at all. It was found to be a solvent for cellulose acetate.

Bases. Aniline will dissolve cellulose acetate,²⁰ but substitution in the amino group reduces solvent power, methylaniline being a poorer solvent than aniline and dimethylaniline a non-solvent.²¹ The behavior of rubber in these liquids is exactly the reverse: aniline hardly swells rubber at all; methylaniline swells it considerably but not sufficiently to lead to dispersion; dimethylaniline is a good solvent for rubber. Benzylamine will dissolve cellulose acetate;²² dibenzylamine has very little solvent power for the ester, it being necessary to raise the liquid to its boiling-point (300°) in order to produce dissolution. Conversely, benzylamine produces only slight swelling of rubber, while dibenzylamine produces considerable.

The influence of an unsubstituted amino group in conferring solvent power for cellulose acetate and destroying it for rubber is seen in the case of anisidine. As already mentioned, anisole is a solvent for rubber and not for cellulose acetate. o-Anisidine, on the contrary, is hardly imbibed at all by rubber, whereas it will dissolve cellulose acetate.

Acids. In the series of fatty acids, too, the rule holds that solvent power for cellulose acetate falls and for rubber rises as the series is ascended. Acetic acid will dissolve the ester, but not rubber, whereas caprylic acid will dissolve rubber, but is only a very poor solvent for the ester. Although the lowest members of the fatty acid series are non-solvents for rubber, the corresponding acid chlorides are good solvents. I find that conversely the acid chlorides will not dissolve cellulose acetate. That is to say: as in the case of the alcohols and glycols, replacement of —OH by Cl ($R.CO.OH \rightarrow R.CO.Cl$) reverses behavior towards cellulose acetate and rubber.

Esters. Methyl acetate, $CH_3.CO.OCH_3$, is a solvent for cellulose acetate,²⁴ whereas it is a precipitant for rubber. Speaking broadly, it may be said that any lengthening of either of the alkyl groups, R or R',

¹⁶ Mardles, *loc. cit.*; *Trans. Farad. Soc.*, **18**, 313 et seq. (1923).

¹⁷ Mardles, *J. Soc. Chem. Ind.*, **42**, 127 (1923).

¹⁸ Marks Eng. Pat. 238,485, Apr. 3, 1925.

¹⁹ Worden, *loc. cit.*, 2681.

²⁰ Fenton and Beiry, *loc. cit.*; Mardles *loc. cit.*

²¹ Mardles, *loc. cit.*

²² Mardles, *loc. cit.*

²⁴ Mardles, *loc. cit.*

in an ester, $R.COOR'$, reduces the solvent power for cellulose acetate and raises the imbibition by rubber. For example, if the R' of methyl acetate is increased to C_4H_9 , solvent power for cellulose acetate is lost, butyl acetate being a non-solvent.²⁵

On the other hand swelling power for rubber rises through ethyl through propyl to butyl acetate, the latter being a solvent. Or consider the case of lengthening the group R . Ethyl acetate is a cellulose acetate solvent and a rubber non-solvent, whereas ethyl butyrate is a non-solvent for cellulose acetate²⁶ and a solvent for rubber.

The influence of an increase in the length of the hydrocarbon residue is to be seen particularly clearly in the case of the esters of dicarboxylic acids. Ethyl oxalate, $(C_2H_5OOC)_2$, will dissolve cellulose acetate,²⁷ but produces hardly any swelling of rubber. Isoamyl oxalate, $(C_5H_{11}OOC)_2$, however, with its longer alkyl groups, fails to dissolve cellulose acetate even on heating to its boiling-point, but swells rubber very considerably. Again, without increasing the ethyl groups of ethyl oxalate, interposition of an alkylene group between the carbethoxy groups causes solvent power for cellulose acetate to fall and imbibition by rubber to rise. Ethyl malonate is still a solvent for the acetate and a poor swelling agent for rubber, and so is ethyl succinate, but ethyl sebacate, $EtOOC.(CH_2)_8.COOEt$, is a non-solvent for cellulose acetate,²⁸ while it swells rubber very considerably.

A similar state of affairs occurs with the esters of dihydric alcohols. The following are imbibed in increasing amounts by rubber, viz.

Ethylene glycol diacetate, $CH_3OOC.CH_2.CH_2.COOCCH_3$,

Trimethylene glycol diacetate, $CH_3OOC.CH_2.CH_2.CH_2.COOCCH_3$,

Ethylene glycol dipropionate, $C_2H_5OOC.CH_2.CH_2.COOC_2H_5$,

Ethylene glycol dibutyrate, $C_4H_7OOC.CH_2.CH_2.COOC_4H_7$,

Trimethylene glycol dibutyrate, $C_4H_7OOC.CH_2.CH_2.CH_2.COOC_4H_7$.

This also represents the order of diminishing solvent power for cellulose acetate. The first two liquids dissolve the acetate readily in the cold. The third causes it to swell in the cold but requires gentle heating to produce solution. The last two liquids require heating to the boiling-point to produce solution, and on cooling the solutions the cellulose ester separates.

Similar relations hold in the case of many other series of esters, increase in the proportion of the molecule represented by hydrocarbon residues leading in general to greater imbibition by rubber.

²⁵ Mardles, *loc. cit.*

²⁶ Mardles, *loc. cit.*

²⁷ Fenton and Berry, *loc. cit.*

²⁸ Cf. Worden, *loc. cit.*, 2697.

Ethers. In general ethers are non-solvents for cellulose acetate and solvents for rubber. As already mentioned, rubber is soluble and cellulose acetate insoluble in mixed alkyl-aryl ethers such as anisole. It was observed, however, that γ -bromopropyl phenyl ether had very little swelling power for rubber; and, on examining the effect of this compound on cellulose acetate, it was found to dissolve the latter.

Di-ethers of the acetal type are interesting. Acetal itself, $\text{CH}_3 \cdot \text{CH}(\text{OC}_2\text{H}_5)_2$, has been described as a non-solvent for cellulose acetate;²⁹ it is a good solvent for rubber. If, however, the more polar compound, methylal, $\text{H} \cdot \text{CH}(\text{OCH}_3)_2$, is examined, it is found to be a non-solvent for rubber and an excellent solvent for cellulose acetate.

Various compounds. Formamide, a liquid with a very high dielectric constant, dissolves cellulose acetate,³⁰ but is not imbibed at all by rubber. Liquid sulphur dioxide is a solvent for cellulose acetate,³¹ but not for rubber.

Behavior of Meta-Styrene to Organic Liquids:

Following the general considerations regarding the influence of the chemical constitution of liquids on the behavior of organophilic colloids which have been outlined in the above comparison of rubber and cellulose acetate, some observations were made on the behavior of meta-styrene in various liquids. And it was found that this colloid, which, like rubber, is a hydrocarbon, in general swells and disperses in liquids of the same types as those in which rubber swells and fails to swell in liquids which are non-solvents for rubber but good solvents for cellulose acetate. In the case of meta-styrene, as in the case of rubber, increase in the length of the hydrocarbon residues present in a given type of organic molecule tends to increase ability to produce swelling and dispersion.

Owing probably to the lower mechanical strength of swollen meta-styrene as compared with that of swollen rubber, meta-styrene usually disperses more easily than rubber. It was found, for example, that, where meta-styrene is insoluble in the lowest member of a given homologous series, it is not usually necessary to ascend the series so far as in the case of rubber in order to encounter a solvent. But this quantitative difference from rubber does not obscure the fact that broadly the same generalizations regarding the relation between chemical structure and swelling power hold for meta-styrene as for rubber. Some examples will serve to illustrate the parallelism between the behavior of meta-styrene and rubber and the contrast between meta-styrene and cellulose acetate.

²⁹ Fenton and Berry, *loc. cit.*

³⁰ Fenton and Berry, *loc. cit.*

³¹ Fenton and Berry, *loc. cit.*

In formamide, acetonitrile, acetoacetic ester, ethyl alcohol, dichlorhydrin, diacetone alcohol, cyclohexanol, ethyl malonate, ethyl oxalate, acetic anhydride, and acetic acid, all of which are solvents for cellulose acetate and non-solvents for rubber, meta-styrene entirely fails to swell. *Ethers.* Meta-styrene dissolves in acetal; less readily in ethylal, and not at all in methylal. It readily disperses in anisole. In the aliphatic ethers its behavior is different from that of rubber, since it swells only very slowly in ethyl ether and not at all in isoamyl ether. *Hydrocarbons.* Like rubber, meta-styrene readily swells and disperses in aromatic hydrocarbons and halogenated hydrocarbons, *e.g.*, in benzene, toluene, xylene, tetrahydronaphthalene, chloroform, carbon tetrachloride, tribromhydrin, bromonaphthalene. But it imbibes aliphatic hydrocarbons hardly at all (Cf. its behavior in aromatic and aliphatic ethers, *supra*). Rubber imbibes aliphatic hydrocarbons to a much smaller extent than aromatic ones, but the difference is by no means so marked as in the case of meta-styrene. Meta-styrene imbibes pinene only slightly. Like rubber, it hardly swells at all in caryophyllene. *Esters.* As in the case of rubber, while ethyl malonate produces no swelling, ethyl sebacate swells meta-styrene and gradually disperses it. As with rubber, swelling generally increases as the length of the hydrocarbon residues is increased. Thus butyl acetate swells and disperses meta-styrene comparatively quickly, whereas after a week at room temperature methyl and ethyl acetates have produced only swelling, not solution. Ethyl butyrate, amyl acetate, and ethyl heptotate all swell and dissolve meta-styrene. Ethyl benzoate, a rubber solvent, also dissolves meta-styrene gradually. *Amines.* As in the case of rubber, swelling power increases in the order aniline-methylaniline-dimethylaniline; and the secondary amines, diethylamine and piperidine, are powerful solvents. *Sulfur compounds.* A striking feature about the behavior of rubber towards organic liquids is that the replacement of oxygen by sulfur often converts a substance with little or no swelling power into a powerful swelling agent and solvent. This is found also to be the case with meta-styrene. Ethyl mercaptan and thiophenol rapidly disperse it. Phenyl isothiocyanate, a good solvent for rubber, is also one for meta-styrene. It is distinguished by giving a comparatively limpid solution. *Aldehydes.* As with rubber, heptaldehyde produces swelling followed by solution; and benzaldehyde swells the colloid more rapidly than salicylaldehyde. *Ketones.* Acetone is imbibed only very slightly by meta-styrene. Methyl ethyl ketone is imbibed to a considerably greater extent, and after seven days at room temperature has dispersed the colloid. Diethyl ketone rapidly swells meta-styrene, and takes it into solution at room temperature within seven hours. *Acids.* The fatty acids are much poorer swelling agents in the case of meta-styrene than in that of

rubber. Butyric acid produces practically no swelling, and even caprylic acid requires a long period at room temperature to produce solution.

Higher Cellulose Esters and Cellulose Ethers:

Still further examples serving to exhibit the interrelation in chemical character between organophilic colloids and their "solvents" are to be found in the higher esters and in the ethers of cellulose, although the amount of data available in this connection is not large.

Stearates and laurates of cellulose were prepared by Grün and Wittka³² by treating cellulose, in the presence of pyridine, with stearyl and lauryl chlorides. In these higher esters the CH_3 groups of cellulose acetate are represented by long hydrocarbon residues, $\text{C}_{17}\text{H}_{35}$ and $\text{C}_{11}\text{H}_{23}$ respectively. These esters are therefore much less polar than cellulose acetate, and accordingly their solubility relationships are different from those of the latter. Cellulose dilaurate and distearate are insoluble in the usual solvents for the ordinary cellulose esters; in epichlorhydrin, dichlorhydrin, and the esters of monocarboxylic acids. They are precipitated from solution by acetone. Cellulose distearate is insoluble in triacetin (a solvent for cellulose acetate), but, as the size of the alkyl groups is increased, its solubility in triglycerides increases. It shows progressively increasing solubility in tributyrin, tri-isovalerin, tricaprylin, etc., and dissolves freely in triolein.³³ It is to be observed that the solubility relations of cellulose stearate are thus in contrast with those of cellulose acetate despite the fact that the degree of acylation is lower in the stearate than in the acetate. The ordinary acetate corresponds approximately to a tri-ester, while the highest stearate prepared by Grün and Wittka was only a di-ester. If a tristearate could be prepared, it would probably be found that the contrast was still more marked. Not improbably cellulose tristearate would dissolve in hydrocarbons. The dilaurate, dipalmitate, and distearate of hydrocellulose (slightly degraded cellulose) prepared by Gault and Ehrmann³⁴ were in fact colloiddally soluble in benzene and other aromatic hydrocarbons. They were also soluble in chloroform and in tetrachlorethane, and were insoluble in acetone, alcohol, and acetic acid.

Cellulose ethers have not yet been studied very fully. They are however presumably less polar than the lower esters; and, in accord with this presumption, it is found that, while cellulose acetate is insoluble in hydrocarbons, cellulose ethers are stated to dissolve in tetra- and deca-hydronaphthalene³⁵ and apparently also in ethyl-

³² *Z. angew. Chem.*, **24**, 645 (1921).

³³ Grün and Wittka, *loc. cit.*

³⁴ *Compt. rend.*, **177**, 124 (1923).

³⁵ U. S. Pat. 1'441,181, Jan. 2, 1923.

benzene.³⁶ It would also appear that they are soluble in dimethylaniline, a liquid in which, as previously mentioned, cellulose acetate is insoluble.

Phytosterolin:

Phytosterolin, a glucoside of sitosterol, was discovered by Power and his co-workers³⁷ in the resin of various plants. It has since been found to occur frequently, although only in small amounts, in vegetable products; it occurs, for example, in such diverse materials as rhubarb, wheat, and rubber. It does not possess a melting-point, but decomposes on heating to a high temperature (ca. 280°). As was observed by its discoverers, it is insoluble in all the ordinary organic solvents, such as alcohol, ethyl acetate, acetone, benzene. The only solvents for it that were encountered by its discoverers were pyridine and hot amyl alcohol.

A further examination of phytosterolin shows that it has the properties of an organophilic colloid. On heating it with a variety of organic liquids, it will swell and then undergo dispersion; and, on cooling, such dispersions often set to firm gels. It is interesting to find that the liquids with which it forms sols and gels are, broadly speaking, similar in type to those in which a hydrocarbon colloid will dissolve. Apparently the large hydrocarbon residue, $C_{27}H_{48}$, of the phytosterol is sufficient to render the molecule one of low polarity despite the presence of five OH groups in the glucose part. Phytosterolin will, for example, disperse and yield gels with amines such as dibenzylamine and dimethylaniline. It will also yield sols and gels with a high-boiling hydrocarbon such as mesitylene and with a high-boiling halogenated hydrocarbon such as α -bromonaphthalene. Other types of liquids in which it will disperse and which are also swelling agents for rubber are mustard oils (*e.g.*, phenylisothiocyanate), higher ethers (*e.g.*, anisole), and higher fatty acids (*e.g.*, caprylic and oleic acids).³⁸ The fact that it will dissolve in fatty acids is of interest as suggesting that in nature it occurs in solution in the fatty acids which usually or always accompany it. In fact it is perhaps the only known naturally-occurring organophilic colloid which occurs in nature in a swollen condition.

Silver Soaps:

While the alkali metal soaps are both hydro- and organo-philic, the silver soaps are only organophilic. And it is interesting to find that, in so far as a first survey of their solubility relationships en-

³⁶ U. S. Pat. 1,467,091, Sept. 4, 1923.

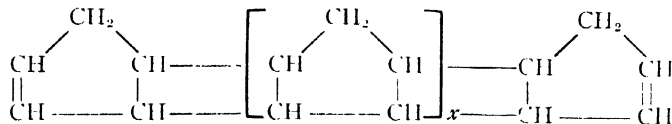
³⁷ *Trans. Chem. Soc.*, 97, 99 (1910); 99, 937 (1911); 103, 399, 1022 (1913).

³⁸ Whitby, Dolid, and Yorston, *Trans. Chem. Soc.*, June, 1926.

ables a general statement to be made, they are dispersable and form gels in liquids of the same types as those which swell rubber and phytosterolin. This may be considered as due to the long hydrocarbon chains which they contain. Silver palmitate, stearate, and oleate swell and disperse on heating them in xylene, and the sols thus formed set on cooling to clear or translucent gels. Silver oleate behaves similarly in benzene, but the palmitate and stearate do not appear to swell sufficiently in boiling benzene for dispersion to take place. Dispersion in organic liquids can be obtained at a lower point in the fatty acid series in the case of the silver than in the case of the alkali metal salts. Thus, silver caproate will disperse in hot xylene and on cooling form a weak gel, whereas sodium and potassium caproates remain undispersed in boiling xylene.³⁹

Molecular Weight of Organophilic Colloids.

Rubber and the cellulose esters, the most fully investigated organophilic colloids and those of greatest industrial importance, are generally supposed to have very high molecular weights; and there is perhaps a tendency to assume that the possession by an organic substance of the ability to swell in suitable liquids, to yield viscous solutions at low concentrations, and to form gels necessarily implies a high molecular weight. That any such assumption is unjustified is proved by the fact that such comparatively small molecules as those of the soaps (*e.g.*, $C_{17}H_{35}COONa$ and $C_{17}H_{35}COOAg$) and of phytosterolin ($C_{60}H_{110}O_6C_{27}H_{46}$) possess the properties mentioned. Another example of an organophilic colloid of known, low molecular weight is one, of considerable interest, afforded by the recent work of Staudinger and Bruson⁴⁰ on the polymerization of cyclopentadiene. These authors have obtained a series of five polymerization steps of cyclopentadiene, of the type



Colloidal properties appeared in the penta-polymer. While tri- and tetra-cyclopentadienes are crystalline solids and give normal values for the molecular weight by the freezing-point method in benzene, penta-cyclopentadiene is an amorphous solid, forming colloidal solutions and giving abnormally high values for the molecular weight by the cryoscopic method. This substance, $(C_5H_6)_5$, has a comparatively small

³⁹ Whitby, *Science*, **53**, 580 (1921); *Trans. Chem. Soc.*, June, 1926.

⁴⁰ *Liebigs Ann.*, **447**, 97 (1926).

molecule, yet its solutions in benzene show the Tyndall phenomenon, and it separates from such solutions on cooling in a gelatinous condition. A 1 per cent solution in hot nitrobenzene gels on cooling.

The mere fact that an organophilic colloid gives high values when the molecular weight is determined by cryoscopy cannot be accepted as sufficient evidence of the possession of a high molecular weight in the sense in which the term is applicable to crystalloids. Staudinger and Bruson's pentacyclopentadiene gave values from $(C_5H_6)_{18}$ to $(C_5H_6)_{40}$, yet molecular weights determined by the ebullioscopic method in chloroform and other evidence showed the molecule to be only $(C_5H_6)_5$. Another case to which reference may be made in this connection is that of the organophilic colloids obtained by heating drying oils alone, with oxygen, or with sulfur. Here too it has been found that the values obtained for the molecular weight by cryoscopy (including Rast's camphor method) vary in a disturbing way with the concentration of the solution.⁴¹ It is of course well known that the figures obtained for the molecular weight of hydrophilic colloids often vary with the concentration, but, as most of such colloids are naturally occurring substances of unknown molecular weight, it is not possible in such cases, as it is in the case of some of the organophilic colloids mentioned above, to compare the figures obtained with the known molecular weight.

Considerations such as those just indicated suggest that it is desirable to exercise great caution in concluding from molecular weight determinations made by the ordinary methods that the molecules (the "chemical" molecules) of rubber and the cellulose esters are necessarily very large.

Swelling. Viscosity.

It would probably not be unfair to say that the property of lyophilic colloids which is fundamental and on which most of the other properties depend is ability to imbibe suitable liquids—to swell. That this is so is perhaps somewhat obscured in the case of hydrophilic colloids and especially in the case of proteins by ionic effects. In the case of proteins a great deal of attention has been devoted to the way in which the *magnitude* of the swelling is influenced by the concentration of hydrogen, hydroxyl, and other ions—not unnaturally, on account of its probable physiological importance. But, even in the case of proteins, the fundamental fact of the occurrence of swelling at all would seem to call for an explanation on lines other than ionic ones; and certainly in the case of the organophilic colloids, especially

⁴¹ *Vide* Seaton and Sawyer, *J. Ind. Eng. Chem.*, **8**, 490 (1916); Friend, *Trans. Chem. Soc.*, **111**, 162 (1917); *J. Oil and Color Chemists Assoc.*, **1924**, Suppl. to **7**, No. 46; Morrell, *ibid.*, **7**, 153 (1924); Whitby and Chataway, *J. Soc. Chem. Ind.*, **45**, 115T (1926).

in the case of hydrocarbon colloids, an explanation of swelling cannot possibly be found in terms of ions.

To make any dogmatic statements as to the fundamental nature of swelling would, in the present state of our knowledge, be premature. Nevertheless, it may be remarked that a consideration of the relations which exist between the chemical character of liquids and their imbibition by a given organophilic colloid, especially by rubber (*vide supra*), make it difficult to resist the conclusion that the process of imbibition by lyophilic colloids is essentially similar to the process of solution in the case of crystalloids, the main difference between such colloids and crystalloids being that in the case of the former the association of the liquid with the solid does not, as in the latter, lead to dispersion of the solid into its individual molecules. In the case of lyophilic colloids, molecules of the "solvent" associate themselves with molecules of the solid by means of residual forces, but this does not have the effect, as it does in the case of crystalloids, of breaking all the bonds which in the original solid united the individual molecules into crystals or other aggregates, and there results swollen (solvated) aggregates of molecules. A view similar to this has recently been expressed by Arsem,⁴² who writes: "When a crystalline substance goes into solution, it seems permissible to assume that the lattice-forming residual valence bonds are separated and appropriated by the superior combining power of the solvent molecules, so that the crystal structure is entirely broken down and the molecules individually dispersed. In a gel [say, a swollen lyophilic colloid], however, some of the residual valences function permanently as lattice bonds while others remain free and can hold or release molecules of free phase in accordance with surrounding conditions. Swelling, then, is the result of the combination of the molecules of a fluid with the free valences of a gel lattice."

In view of the fact that in the swelling of a colloid the association of the liquid with the solid is, as it were, arrested before it has brought about the dispersion of the solid to its molecular units, it is not perhaps extravagant to say that a study of the forces involved in imbibition by colloids should go a considerable way towards elucidating the process of solution of crystalloids.

In addition to considerations regarding the relation between the chemical character of organophilic colloids and that of the liquids which they will imbibe, there are some other considerations which suggest that swelling bears a similarity to solution. There exists a very broad relationship between dielectric constant and swelling power for organophilic colloids, although, as Mardles⁴³ has pointed out in

⁴² *J. phys. Chem.*, **30**, 806 (1926).

⁴³ *J. Soc. Chem. Ind.*, **42**, 127T (1923).

the case of cellulose acetate, there is far from being an exact parallelism. The broad relation between dielectric constant and swelling power is best seen in the case of rubber. Rubber, a hydrocarbon, has a low dielectric constant, and, speaking broadly, swells most in liquids of low dielectric constant. In the course of our work on the swelling of rubber it has repeatedly been found that the possession of swelling power on the part of liquids could be predicted on the strength of this generalization. Thus, for example, following it, stannic chloride, arsenic chloride and especially silicon tetrachloride were discovered to be good swelling agents for rubber. The extent to which a number of given liquids will swell rubber is not usually in the exact order of the dielectric constants if the liquids belong to different chemical classes, but in a homologous series the order of swelling power is generally inversely that of the dielectric constants. The existence of a relation, albeit only a broad one, between dielectric constant and swelling is in accord with the view that swelling is similar to solution. (Regarding the relation between dielectric constant and solvent power for crystalloids, see *e.g.*, Walden and Werner, *Zeit. physikal.*, 1924, 111, 465.)

In opposition to the idea of Fenton and Berry⁴⁴ that a simple relation exists between high dielectric constant and solvent action on cellulose acetate, Mardles⁴⁵ has urged the fact that, whereas dielectric constant diminishes with rise of temperature, solvent action increases. A similar argument from the effect of temperature on solvent action, if applied to rubber, however, would tend to support rather than oppose the idea of a relation between dielectric constant and solvent action. For it would run as follows: a low dielectric constant in a liquid is favorable to swelling; rise of temperature reduces the dielectric constant; it should therefore (as in fact it does) increase swelling. The case would, however, be more correctly viewed in another way. The fact that rise of temperature favors swelling and dispersion both of cellulose acetate and of rubber should, it would seem, be read as arguing generally that the swelling process is essentially one of solution, for we know in the case of crystalloids that rise of temperature almost invariably favors solution, whether the solute is one which dissolves most freely in liquids of low dielectric constant (*e.g.*, hydrocarbons) or in liquids of high dielectric constant (*e.g.*, ethyl alcohol).

Reference may be made to the work of Knoevenagel and Motz⁴⁶ on the distribution of various swelling agents for cellulose acetate between the colloid and water in which the colloid was shaken. Working with aqueous solutions of aniline, phenol, and ethyl tartrate,

⁴⁴ *Loc. cit.*

⁴⁵ *Loc. cit.*

⁴⁶ *Kolloidchem. Beihfte*, 13, 194 (1921).

these authors found the distribution of the swelling agent to follow the law (Henry's) applying to the distribution of a common solute between two immiscible liquids. This result suggests that imbibition by cellulose acetate is essentially a process of solution.

Consider now the question of the rôle of solvation in the viscosity of sols of organophilic colloids.⁴⁷ Although the electrical charges on the particles may play a certain part in the viscosity of such sols,⁴⁸ they apparently never play more than a comparatively small part. And the question arises as to whether the major rôle in the viscosity of sols of organophilic colloids is to be ascribed to solvation or to some other cause, such as, *e.g.*, the existence of structure in the system. In the case of sols of nitrocellulose, McBain⁴⁹ has recently expressed the opinion that the high viscosity is due for the most part, not to true solvation, but rather to the immobilization of solvent owing to its being enmeshed in a loose structure formed by cohering and ramifying rigid colloid particles or micelles. He bases this opinion in part on the fact that sorption experiments show the degree of solvation of nitrocellulose to be not more than 100 per cent of the weight of the nitrocellulose—a degree altogether too small to account for the observed viscosities.

There is reason to believe in the case of certain other and probably in the case of many other organophilic colloid sols that the degree of solvation is much greater than that just mentioned, and consequently that solvation plays an important if not a major part in producing high viscosities. For example, rubber can readily be ascertained to imbibe 2000-4000 per cent of its weight of solvent when placed in certain liquids. When raw rubber is immersed in a liquid of high swelling power, *e.g.*, benzene, o-dichlorobenzene, carbon tetrachloride, it will be found to have increased in weight 20-40 times after 24 hours; it will thereafter gradually lose weight owing to diffusion of the swollen rubber into the liquid. And the actual degree of solvation of rubber by good swelling agents is almost certainly even higher than the increase in weight when a piece of rubber is immersed in the liquid, since diffusion of the solvated rubber out of the swollen gel begins before the piece as a whole has reached its maximum swelling.

In addition to that obtained from measurements of swelling, it seems possible to get some light on the solvation of rubber in its sols in certain other ways. On examining a benzene solution of rubber with the dark field condenser, it is impossible to discern particles

⁴⁷ It is hoped to discuss the rôle of solvation in the gelation of sols of organophilic colloids in a later paper on the silver soaps.

⁴⁸ Cf. Krøyt and Eggink, *Proc. Roy. Acad. Rotterdam*, **28**, 43 (1923); Whitby and Jane, *Second Colloid Symposium Monograph*, 1925, 16; de Vries, *Archief voor de Rubbercultuur*, **9**, 294 (1925).

⁴⁹ *J. phys. Chem.*, **30**, 239 (1926).

of disperse phase, but if the solution is subjected for some time to heat or to ultra-violet light (agencies which have the effect of reducing the viscosity), it becomes possible to see particles under the microscope. Or again, if a precipitating liquid of suitable composition is added gradually to the solution, a stage is reached at which a strong Tyndall effect is observable; and at this point particles are visible with the dark field condenser. Further, if, after the point just mentioned has been reached, more of the precipitating liquid is added, a turbidity appears, indicating the onset of precipitation. If the liquid is now allowed to stand undisturbed for several hours, the precipitate which was responsible for the turbidity settles as an "oily" layer, which consists of rubber swollen with a large amount of benzene (very approximately of the order of 10 times the weight of the rubber).

In order to explain such observations, it would appear to be necessary to suppose the rubber in the original solution to be solvated to a very high degree, so that the refractive index of the disperse phase is practically identical with that of the medium, and so that only when de-solvated to a considerable extent do the particles differ sufficiently from the medium in refractive index to be microscopically visible. If the main difference between the original viscous solution and the de-viscified solution was, following McBain's view of the nature of solutions of nitrocellulose, not a large difference in the degree of solvation, but a difference in the extent of coherence and ramification of the micelles, there would seem to be no reason why, if the disperse phase is visible in the latter solution, it should not also be visible in the former.

The fact that the turbidity-producing precipitate mentioned in the penultimate paragraph consists of rubber with a large proportion of benzene is direct evidence that the rubber particles in solution are highly solvated. It would appear that the minimum degree of solvation necessary to maintain rubber in colloidal solution in benzene is of the order of 1000 per cent. In the original, viscous solution the degree must be very much higher than this.

In the case of most organophile colloids it is not so easy as in the case of rubber to secure a reasonably exact idea of the magnitude of the solvation in good swelling agents by direct measurements of the imbibition by pieces of the solid immersed in the liquid, owing to the fact that the swollen colloid has such little mechanical strength that diffusion from the surface begins or disruption occurs long before the piece as a whole has imbibed as much liquid as that corresponding to the weight of colloid which the piece represents. Nevertheless, direct swelling experiments with acetocellulose made by Knoevenagel and Bregenzer⁵⁰ show that this colloid is capable of

⁵⁰ *Kolloidchem. Beihefte*, 13, 262 (1921).

imbibing comparatively large amounts of suitable liquids. For example, they found that when placed in a mixture of nitrobenzene and alcohol (8:2) a chloroform-soluble acetocellulose imbibed 592.6 per cent when in film form and 818 per cent when in powder form.

It was found by the authors just mentioned that liquids which produced greater swelling prior to dispersion gave more viscous solutions than liquids which produced smaller swelling. The well-known fact that the influence of H-ion concentration on the imbibition of water by gelatin and on the viscosity of solutions of gelatin run approximately parallel may also be noted as indicating that solvation plays an important rôle in the viscosity of sols of lyophilic colloids.

Elasticity.

An understanding of the cause or causes of elasticity in lyophilic colloids would be of great value, especially in the case of rubber—the elastic colloid *par excellence*. There is a general apprehension that elasticity in organic materials necessarily connotes a two-phase (solid-liquid) system. Poole, from his recent illuminating investigations of the elasticity of gelatin jellies⁵¹ and of cellulose acetate jellies⁵² concludes that these jellies are two-phase systems. Such jellies, however, formed by first dissolving a colloid and then cooling the solution, are not necessarily strictly comparable with either raw or vulcanized rubber. They do not approach rubber in their degree of elasticity. (I here use the term elasticity, not merely as denoting the magnitude of Young's modulus, but in the fuller, albeit more popular, sense of connoting the capability of being deformed by comparatively small stresses [*i.e.*, small compared, *e.g.*, with the stresses required to deform metals] and of recovering quickly and practically completely from deformation when the stress is removed. "Good" elastic properties in this usage imply, not merely or necessarily a high Young's modulus, but rather a combination of high extensibility and high ultimate tensile strength, such as, *e.g.*, is found in rubber in its optimum state of vulcanization. A cellulose acetate jelly may have a modulus of elasticity as high as that of vulcanized rubber strained to the same extent. Its elastic properties are, however, vastly inferior to those of rubber, because it is not so extensible. Thus Poole⁵³ found a 20 per cent jelly of cellulose acetate in benzyl alcohol to have a modulus of 4.2 kg./cm.² at 56 per cent breaking elongation. This is of the same order as the modulus of a pure gum vulcanized rubber at the same elongation. The rubber could, however, be stretched, say, 800 per cent before it broke, and its ultimate tensile strength might be, say, 300 kg./cm.²)

⁵¹ *Trans. Farad. Soc.*, **21**, 114 (1925).

⁵² *Trans. Farad. Soc.*, Mar., 1928.

⁵³ *Trans. Farad. Soc.*, Mar., 1928.

Raw rubber, even when entirely free from the resin and protein which naturally accompany it, is still highly elastic. It certainly contains no free liquid phase. And it seems to me doubtful whether it can be considered as a two-phase system in the ordinary sense of the term. If different phases are in fact present, it would appear that the less rigid phase or phases can only be a part of the hydrocarbon less highly polymerized than the rest. And the chemical and physical properties of this less highly polymerized part must be so similar to those of the more highly polymerized part that the two parts must be associated so closely, the higher polymer being, as it were, solvated by the lower, that they do not represent two separate phases in the ordinary sense of the term.

In this connection some observations made with meta-styrene seem to be illuminating. Meta-styrene is a hard solid. In massive pieces or films it is clear; as precipitated, white. It shows no evidence of the possession of elastic properties: the films are brittle, and the powder friable. Yet it acquires elastic properties when swollen. If it is precipitated, *e.g.*, by acetone or alcohol, from a solution in, *e.g.*, xylene, benzene, or chloroform, the fresh precipitate is strikingly elastic; it is reminiscent of raw rubber; it is even more extensible than raw rubber, and it recovers from extension with a "snap." If the precipitated material is allowed to stand in the air, it gradually loses its extensibility, and when all the solvent has evaporated the remaining meta-styrene is white and friable. That is to say: while in a swollen condition, meta-styrene is elastic; when unswollen, it is hard and brittle. A permanently elastic material can be obtained by incorporating with meta-styrene a non-volatile swelling agent, *e.g.*, tricresyl phosphate or isoamyl phthalate. As showing that a swollen condition is necessary for the appearance of elasticity in meta-styrene, it may be mentioned that an inextensible material is obtained if, instead of a swelling agent, a non-volatile liquid without swelling properties is incorporated with meta-styrene. Such a liquid is cyclohexanol or high-boiling paraffin (*e.g.*, "Glycoline"). Both these liquids are so completely lacking in swelling power for meta-styrene that they will precipitate it from solution. And if they are incorporated with meta-styrene, the product is inelastic.

Here then is a case of a rigid organophilic colloid which can be rendered elastic, not by causing it to form the solid phase in a solid-liquid system (the case of meta-styrene + cyclohexanol), but by merely causing it to swell. In writings on the two-phase nature of elastic gels, a solvated solid phase has been regarded as a single phase, free liquid being the other phase. "Elastified" meta-styrene is then, in this accepted sense, a one-phase material.⁶⁴

⁶⁴ Prof. R. O. Herzog has kindly undertaken to subject "elastified" meta-styrene to X-ray examination.

It would seem that, although elastic jellies, such as those from gelatin and cellulose acetate, may be two-phase systems, elastic colloids such as rubber and "elastified" meta-styrene, which are distinguished from elastic materials of the first class by their much greater elastic extensibility, are not two-phase systems, at all events in the same sense.

The so-called plasticizers often used along with cellulose esters, with such objects as reducing brittleness and increasing flexibility, are probably "elastifiers," using this term in the sense indicated above in connection with meta-styrene; that is to say, they are non-volatile swelling agents used to improve the extensibility of the esters.⁵⁵

Another elastic colloid to which reference may be made in this connection is the gel obtained by heating a drying oil with sulfur.⁵⁶ A liquid, which consists of unpolymerized or insufficiently-polymerized sulfurized oil, and which might be regarded as a free liquid phase, can be removed from such gels (by, *e.g.*, extraction with acetone) without rendering the colloid inelastic. The remaining, elastic material is probably not a solid-liquid system but a single phase system in the above sense. It probably consists of a number of glycerides to which sulfur has been added and which have subsequently undergone polymerization. (The sulfurized oil gels possess little or no extensibility. This is probably due to a lack of coherency in the structure, which causes tearing to start as soon as stress is applied. Compression tests, however, show them to possess considerable elasticity.)

Another phenomenon the further investigation of which may also throw light on the cause of elasticity in colloids may be mentioned, *viz.*, the influence of change of temperature in causing the appearance or disappearance of elastic properties. Certain colloids, although rigid and brittle at room temperature, if heated acquire elastic properties, which they lose again if cooled. Examples of such colloids are meta-styrene, caoutchouc hydrochloride,⁵⁷ and certain synthetic caoutchoucs mentioned by Ostromislenski.⁵⁸

Among other phenomena which a complete theory of the nature of elastic colloids, especially of rubber, should explain are (a) creep and elastic after-effect, (b) the Joule effect, (c) the manner in which Young's modulus changes as the material is strained *i.e.*, the shape of the stress-strain curve, (d) the high hysteresis. Poole,⁵⁹ who concludes from his investigations of cellulose acetate jellies that such jellies consist of a solid phase of solvated fibrils together with a liquid phase, refers to "reversible solvation" in his explanation of creep

⁵⁵ Cf. Gardner and Parks, *U. S. Paint Manfrs. Assoc. Circ.* 234, 260 (1925), quoted *Ann. Repts. Prog. Appd. Chem.* 10, 370 (1925).

⁵⁶ Whitby and Chataway, *J. Soc. Chem. Ind.*, 45, 115T (1926).

⁵⁷ Cf. Whitby and Jane, *Trans. Roy. Soc. Canada*, 20, 130 (1926).

⁵⁸ *J. Russ. Phys. Chem. Soc.*, 47, 1374 (1915).

⁵⁹ *Trans. Farad. Soc.*, Mar., 1926.

and elastic after-effect. It is difficult to believe that reversible solvation can explain creep and elastic after-effect in highly extensible elastic colloids such as rubber and "elastified" meta-styrene, in which, we have seen reason to believe, a liquid phase is lacking. Further, it seems improbable that mere stretching, even if repeated, will produce any de-solvation in the case of such colloids, as otherwise it might be expected that stretching a piece of vulcanized rubber which had been swollen to a certain extent would produce syneresis. No such syneresis is observable. It seems more likely that the explanation of creep, elastic after-effect, recovery from sub-permanent set, and the Joule effect in rubber is to be sought, not in reversible solvation, but in orientation of the micelles. In this connection the observation of Katz⁶⁰ that rubber shows an X-ray diffraction pattern when stretched is suggestive.

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⁶⁰ Katz and Bing, *Z. angew. Chem.*, **38**, 439 (1925); Katz, *Kolloid Z.*, **36**, 300 (1925).

COLLOIDAL PROPERTIES OF THE SURFACE OF THE LIVING CELL.

By J. F. McCLENDON

It was shown by Mauritz Traube¹ that colloidal membranes may be formed by the interaction at the zone of contact of two mutually precipitating solutions; for instance a solution of copper sulfate and one of potassium ferrocyanide forming a colloidal membrane of copper ferrocyanide. Such membranes have been extensively studied by H. N. Morse at Johns Hopkins University, who used them as semi-permeable membranes in the measurement of the osmotic pressure of sugar solutions. Morse showed that when the membrane lost its colloidal structure its semi-permeability was lost. For instance, if the membrane was treated with a solution of potassium chloride it lost its semi-permeability to sugar, and on microscopic examination, small crystals of copper ferrocyanide could be observed in the membrane; in other words, when it changes from a colloidal to a crystalline structure, or perhaps when the size of the crystals exceed the colloidal dimensions, semi-permeability is lost. Many other colloidal membranes have been used; for instance, Pascucci² made colloidal membranes out of lecithin and cholesterol supported by silk. He showed that the permeability depended on chemical composition and that these membranes showed a certain similarity to the membranes on the surface of red blood cells. Since $\frac{1}{3}$ of the ghost of the red blood cell, that is, the part that remains after the diffusing out of the hemoglobin and salts, is lecithin plus cholesterol and the ratio of lecithin to cholesterol varies in different animals, and that the stability of the plasma membrane in blood cells of these animals is related to the stability of the artificial membrane with the same ratio of lecithin to cholesterol, the analogy is very suggestive. D. T. MacDougal³ has for a number of years been studying colloidal membranes and their relation to the growth of plants.

It seems certain that the surface of the living cell is of a colloidal nature. Viewed with the ultra-microscope, the surface of a red blood cell, for instance, appears as a polished mirror, whereas the interior of the cell is optically void unless it has been injured. It doesn't

¹ *Arch. Anat. Physiol.*, **87**, 609 (1867).

² *Beitr. chem. Physiol. u. Pathol.*, **6**, 543 (1905).

³ *Proc. Am. Phil. Soc.*, **62**, 1 (1923).

seem possible to study the membrane by means of the ultra-microscope. Some side-light on its chemical nature might be gotten from taking a large mass of well washed cells and dissolving off a very small amount of this membrane material and analyzing it. B. Hansteen Cranner⁴ has attempted to do this with plant cells. As is well known, the membrane on the surface of plant cells is in two layers, one the so-called cell wall and another layer, the plasma membrane, just beneath the cell wall, which can be pushed away by the osmotic pressure of substances that can penetrate the cell wall but not the plasma membrane. Cranner was able to dissolve out phytosterols and pectins by means of distilled water. Apparently he supposes that these substances form not only the plasma membrane but also extend through holes in the cellulose cell wall. He supposes the plasma membrane to be a mosaic of phytosterol and pectin. Pectin probably enters quite generally in the surface composition of cells and the insolubility of its calcium salt probably helps to keep it in place. Herbst⁵ showed that removing calcium from the medium caused cells to fall apart and it would seem possible that something like calcium pectate or a similar compound is necessary for sticking them together and hence enters into the surface composition. The importance of pectins in plants is shown by the presence of three so-called pectic enzymes in plants (2 concerned with sol \longleftrightarrow gel change and 1 with hydrolysis). F. H. Scott⁶ showed that protein could be washed away from red blood corpuscles by means of isotonic Ringer's solution. It is not clear whether this protein enters into the composition of the semi-permeable layer at the surface or not. Lepeschkin⁷ and Ruhland⁸ and many others have studied the colloidal properties of the so-called plasma membrane or semi-permeable surface layer of the living cell. It is well known that Overton investigated the permeability of this layer. He studied roughly the rate of penetration of over five hundred carbon compounds and many other substances. From a modern viewpoint his results may be summed up as indicating that the cell is impermeable to polar compounds. In regard to non-polar compounds, if one weakly polar group such as the hydroxyl is present, the compound may enter the cell without difficulty. In general, the rate of entrance seems to be proportional to the ratio of the number of non-polar groups to the polar groups. Overton's work has been corrected as to detail and extended by numerous investigators. It was attempted to measure the penetration of substances by putting cells in solutions of these substances and taking the cells out and analyzing them.⁹ This method

* Meldinger Norges Landbruksskole (Kristiana) (II), 11 (1922).

* Herbst, *Arch. Entwicklungsmech.*, 17, 440 (1904).

* *J. Physiol.*, 50, 128 (1915).

* *Kolloid-Z.*, 13, 182 (1913).

* *Ber. deutsch. bot. Ges.*, 31, 304 (1913).

* McClendon, *Am. J. Physiol.*, 27, 265 (1910); also many authors using dyes.

was made somewhat uncertain by the possibility of adsorption. Another method was used by Wodehouse¹⁰ who found a single cell of the seaweed *Valonia*, with a large vacuole, containing up to 5 cc. of cell sap. Analysis of the contents of this vacuole showed it to differ considerably from the sea water in composition. In a similar fresh water plant, *Nitella*, Hoagland, and Davis¹¹ showed that this cell could concentrate the ions of pond water from 10 to 870 times, and since the ratio of the concentration of cations on the outside of those on the inside varied for each cation, it is difficult to explain such a relation on the basis of a Donnan effect. Many observations have been made on the exosmosis of electrolytes from cells. It was shown by the writer¹² that the eggs of certain fresh water and brackish water fish when developing in distilled water do not lose any of their salts to the water, but they lose salts to unbalanced salt solutions or solutions of toxic substances. Gray¹³ showed that the egg of the trout does not lose electrolytes to the water in which it is developing unless it is injured or dies in which case the outward diffusion of electrolytes causes the globulins of the eggs to precipitate. When this egg is placed in solution of electrolytes, this globulin dissolves.

Perhaps the red blood corpuscle is the animal cell that has been mostly studied. The older analyses of Abderhalden and of Schmidt and numerous recent analyses have shown that there is about seven times as much sodium in the plasma as in the corpuscle. There is about twenty times as much potassium in the corpuscle as in the plasma and there is about twice as much chlorine in the plasma as in the corpuscle, but this value is quite variable owing to the rapidity of the chloride shift. In 1867 Zuntz showed that the titratable alkali of the serum increased when CO_2 was passed into defibrinated blood. In 1874 it was further shown that when CO_2 passes into defibrinated blood the chloride ion of the serum passes into the corpuscles. The osmotic pressure of the corpuscles is increased and it swells. In 1897 Köppe proposed an ionic exchange theory which was later modelled by Spiro and Henderson. The question was taken up recently by Warburg, Henderson, Van Slyke and their collaborators. The chloride shift is definitely established. (The author has evidence for the chloride shift in other cells.) In other words, the corpuscle is permeable to Cl ions but not to K or Na ions. But this does not give us any idea of the rate of the passage of ions through the plasma membrane.

For further consideration of permeability the reader is referred to Jacobs¹⁴ and Lillie.¹⁵

¹⁰ *J. Biol. Chem.*, 29, 453 (1917).

¹¹ *J. Gen. Physiol.*, 5, 629 (1923).

¹² McClellon, *Am. J. Physiol.*, 29, 296 (1912); 38, 173 (1915).

¹³ *J. Physiol.*, 53, 308, 322 (1920).

¹⁴ Sec. III of Cowdry, "General Cytology," U. of Chicago Press, 1924.

¹⁵ Lillie, R. S., "Protoplasmic Action and Nervous Action," U. of Chicago Press, 1928.

It appeared to the writer that the electric conductivity method should be adaptive to the determination of the rate of the passage of ions. G. N. Stewart¹⁶ showed that the corpuscles acted as insulators. Similar observations were made by the writer¹⁷ on sea urchin eggs, and it was further observed that the electric conductivity of the eggs was increased when fertilized or stimulated to develop by treatment with acetic acid. In this case the acetic acid or excess spermatozoa were washed off with sea water and the egg mass precipitated down to the original volume and brought back to original temperature on making further determinations of conductivity. Similar results were obtained on striated muscle.¹⁸ By means of an analytical method it was shown theoretically that the change in the shape of the muscle fibers would not make a difference in the electric conductivity if the proper precautions were used.

The physiologist is in the position of an arbitrator between the observations made from a chemical and physical standpoint on the material he uses and observations on the function of these materials which in the minds of different people might lead to discordant ideas. We have on the one hand the colloidal cell surface or plasma membrane; on the other hand we have the cell as a spatial individual and sometimes as an irritable element. The continued separate existence and the response to stimulation are associated according to the above observations with the colloidal properties and some colloidal change in the plasma membrane. The theoretical significance of such a relation was elaborated by R. S. Lillie.¹⁹ On the basis of these electric conductivity experiments the writer gave two lectures at Woods Hole on this subject.²⁰ Osterhout has extended this conductivity method and compiled the results in book form.²¹ The writer was not satisfied with the technique of these early experiments and has repeatedly returned to this work in an attempt to improve them. Höber²² made some early experiments on the conductivity of blood and muscle using radio-frequency damped waves.

In the use of the alternating current one is not measuring resistance alone but what is called by electrical engineers, the impedance of the circuit. The writer showed²³ that in a Wheatstone bridge arrangement, if a condenser is placed parallel with the standard resistance as is often used in producing a sharp null point in the method, and if the capacity of this condenser is called the "parallel capacity" of the con-

¹⁶ *Zent. Physiol.*, 11, 332 (1897).

¹⁷ McClendon, *Science*, 32, 122 (1910); *Am. J. Physiol.*, 27, 250 (1910).

¹⁸ McClendon, *Am. J. Physiol.*, 29, 302 (1912); *Biol. Bull.*, 22, 133 (1912).

¹⁹ *Biol. Bull.*, 17, 188 (1909).

²⁰ McClendon, *Biol. Bull.*, 22, 133, 155 (1912).

²¹ Osterhout, "Injury, Recovery, and Death in Relation of Conductivity and Permeability," Lippincott (1922).

²² *Arch. ges. Physiol.*, 133, 237 (1910); "Physikalische Chemie der Zelle und Gewebe," 5th Ed., Leipzig (1922).

²³ McClendon, *Sci. Proc.* xiv, *J. Biol. Chem.*, 41, 66 (1920).

ductivity cell and material it contained, the parallel capacity of the conductivity cell filled with blood was greater than that when filled with distilled water and values of the parallel capacity were given in microfarads. Such measurements have been greatly extended by Hugo Fricke.²⁴ It was shown by the writer²⁵ that the use of such a parallel capacity when the various properties of the circuit including the conductivity vessel were unknown might lead to errors. It was therefor advocated to obtain a sharp null point by placing a variable inductance in series with the conductivity vessel.

During the last six years, the Wheatstone bridge and other apparatus used in these measurements have been completely rebuilt five times. All the improvements were not possible to apply at the beginning owing to the fact that some of them had to wait on improvements in radio engineering and a supply of parts on the market. We did not make our own electron tubes and found difficulty in obtaining proper ones at first. The apparatus as now used consists of an oscillator the frequency of which can be varied from 260 to 10,000,000 cycles per second and Wheatstone bridge for high and low frequencies. In the simplified Wheatstone bridge the detector circuit is connected by means of a toroidal transformer, a grid coupled circuit, an electron tube detector circuit and heterodyne oscillator, and the beat note is amplified by a two-stage amplifier and heard in a telephone. The greatest recent improvements in the apparatus have been in the complete shielding, universal use of toroidal inductances and the compact form of the constant temperature regulation. Every section of the apparatus is placed in a copper box. All these copper boxes are grounded. The distributed capacity losses are minimized by having the boxes large and the apparatus separated by considerable distance from the walls of the box. The apparatus used to maintain constant temperature is in the same copper box (covered with 2 inch felt) with the conductivity cell but at the moment of making a determination all parts of this apparatus are grounded by turning a multiple pole double throw switch. Besides the measurements with this apparatus, numerous measurements have been made by means of direct current.²⁶ The determination of ratio of the volume of the corpuscles to that of the serum was determined by means of a hematocrit directly connected to a Dumore motor rotating at 20,000 revolutions a minute inside a vacuum chamber. Some determinations were made on corpuscles without any serum whatever between them. An analysis of the results showed that such a mass of corpuscles behaved as a series parallel circuit with an average total impedance of 880 ohms and a reactance such that an inductance of an average of 0.89 millihenry had to be placed in series with it in order

²⁴ *Physiol. Rev.*, **26**, 682 (1925).

²⁵ McClendon, *J. Biol. Chem.*, **43**, 817 (1920).

²⁶ McClendon, *J. Biol. Chem.*, **68**, 653 (1926).

to produce resonance. A model of a similar circuit may be made as follows: the two plates of a condenser of 1500 micro-microfarads are short circuited by means of a parallel resistance of 675 ohms and in series with the condenser is placed a resistance of 200 ohms. The total impedance of this circuit at 1000 cycles per second is 874.3 ohms and the inductance which must be placed in series with it is 0.68 millihenry. The condenser represents the capacity of the plasma membrane, Figure 1. The resistance of 675 ohms represents the resistance of the plasma membrane; that is to say, the plasma membrane behaves as a leaky condenser. The resistance of 200 ohms represents the resistance of the interior of the blood corpuscle. In other words, the resistance of the plasma membrane is three times as great as the resistance of half the cell interior. (Half is used because there are two plasma membranes, one at entrance and one at exit of the current, and we may consider half the cell as one plasma membrane and half the cell interior.) Since the thickness of the plasma membrane is very small compared with the thickness of the cell, the relative speed of an ion through it is very small.

TABLE I
WHEATSTONE BRIDGE MEASUREMENTS ON BEEF BLOOD CELLS AT 1000
CYCLES PER SECOND

Z (cells)	Z (serum)	$\frac{Z_c}{Z_s}$	Z (laked)	$\frac{Z}{Z \text{ (laked)}}$	I (cells)
708.2	70.3	10.1	—	—	0.54
714.2	62.4	11.5	174.4 D. C.	4.10	0.57
854.6	71.8	11.9	196.0 Sap	4.36	1.07
892.8	69.2	12.9	212.8 "	4.20	0.76
914.4	81.5	11.2	219.1 "	4.17	0.79
1,002.9	66.4	15.1	202.3 "	4.96	1.19
1,049.1	63.7	16.5	- "	—	1.31
Average 880.3	69.3	12.7	200.9	4.36	0.89

In the above table the first column gives the specific impedance Z of the closely packed cells, the second column the specific impedance of the serum, the third column the impedance of the cells taking the impedance of the serum as unity. In the fourth column is given the specific impedance of the same mass of cells that have been laked or hemolyzed (that have had the plasma membrane destroyed); in the fifth column the impedance of the normal cells on the basis of the impedance of the hemolyzed cells taken as unity, and in the sixth column, inductance that must be placed in series with the conductivity vessel for resonance. Some of the cells (D. C.) were laked by passing direct current of 110 volts through them for twenty minutes, reversing the direction of the current every minute. After the experiment was over, the laked mass

was mixed with serum and observed under the microscope. Laking was not complete, as cell fragments could be observed. In the other cases (Sap.) the cells were laked with saponin. Microscopic examination later showed hemolysis to be complete. The resistance, however, was as low after laking with direct current as after laking with saponin. The impedance of the intact cells was found to be four to five times

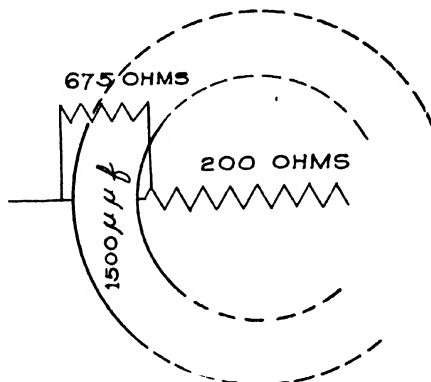


FIG. 1.

as great as that of the hemolyzed cells. If we may assume that the impedance of the hemolyzed cell is the same as the resistance of the cell interior of the intact cell, then at least three-fourths of the impedance is due to the plasma membrane.

TABLE II

f	C	R_1	R_2	Z	L
500	1,500 MMf.	675	200	874.5	0.68
1,000	"	"	"	874.3	0.68
1,000,000	"	"	"	216.3	0.0165

The above table shows values obtained on a model of the cell as shown in Figure 1. The impedance due to the plasma membrane is almost as great as the resistance of the plasma membrane; thus the total impedance is 874.3 ohms at 1000 cycles per second. This model is made up of the resistance of the cell interior which is 200 ohms and the impedance of the plasma membrane which would be 874 minus 200 ohms or 674 whereas the resistance of the plasma membrane is 675 ohms, a difference of less than one-sixth of one per cent between impedance and resistance of parallel circuit. We may conclude, therefore, that the electric current carried by the Cl^- ions passing through

the plasma membrane is less than one-third as great as the electric current carried by the ions in the cell interior in their diffusion inside the cell. If serum is added to blood corpuscles, say we have a mixture as in blood, another parallel circuit, the resistance represented by the serum, is introduced into the system. The less the resistance of the serum, the less the impedance of the total circuit and the less the ratio of the impedance of blood to that of serum as represented in Table II.

TABLE III
SPECIFIC VALUES OF IMPEDANCE OF BEEF BLOOD AT 25°

Cell Volume Per Cent	$f = 1000$ Z_B/Z_S	$f = 1,000,000$ Z_B/Z_S	Z_{1000} $Z_{1,000,000}$
96.8.....	25.0	6.3	4.0
96.6.....	19.0	5.7	3.5
96.2.....	17.6	5.4	3.3
95.8.....	18.8	—	—
95.2.....	16.0	6.4	2.5
94.2.....	19.0	6.7	2.8
94.2.....	15.0	5.5	2.7
94.2.....	13.9	5.2	2.7
94.2.....	13.7	5.4	2.5
93.9.....	16.7	5.4	3.0
93.1.....	14.0	—	—
93.1.....	13.9	5.5	2.5
92.4.....	15.5	5.9	2.6
91.8.....	16.0	5.2	3.0
91.0.....	11.0	5.3	2.2
90.8.....	12.7	5.2	2.4
90.4.....	11.0	5.0	2.2
87.6.....	10.1	5.0	2.0
86.5.....	9.7	5.0	1.9
77.1.....	5.8	4.0	1.5
76.4.....	6.5	4.2	1.3
72.1.....	4.7	3.6	1.3
67.3.....	3.9	3.0	1.3
65.4.....	4.0	3.2	1.25
65.1.....	3.8	3.1	1.23
64.9.....	4.0	3.2	1.25
61.1.....	3.3	2.8	1.18
55.7.....	3.1	3.0	1.03
42.3.....	2.0	2.0	1.00
42.2.....	2.1	1.95	1.08
41.5.....	2.0	1.90	1.05
39.6.....	2.1	1.92	1.10
37.3.....	1.9	1.87	1.01
24.6.....	1.3	—	—
22.0.....	1.4	1.40	1.00
19.7.....	1.45	1.45	1.00
19.0.....	1.4	1.40	1.00

In Table III it is shown that the ratio of the impedance of blood at a thousand cycles to that at a million cycles increases at first slowly as the cell volume rises above 25 per cent, and increases very rapidly as the cell volume rises above 95 per cent. At 96.8 per cent cell volume

the impedance is four times as great at a thousand cycles as it is at a million cycles. Unfortunately, we did not make any very accurate determinations at a million cycles of the impedance of a mass of pure corpuscles. Furthermore, as shown by comparison of Table III with Table I, the impedance of the pure mass of cells on the basis of serum as unity $\left(\frac{Z_c}{Z_s}\right)$ is lower than that of the blood with 96.8 per cent cell volume. This is probably due mainly to the injury of the cells in packing them down in such close proximity. It is not due entirely to temperature difference as the temperature in Table I was close to 25° and that in Table III was kept constant at 25° + 0.1°.

Assuming beef corpuscles are 0.0048 mm. in diameter and 0.002 mm. in thickness, and with random arrangement, assuming an average diameter of 0.003 mm., there would be about 3,000 corpuscle layers in a centimeter cube from top to bottom, or about 6,000 plasma membrane layers. Since the value of the specific capacity shown in Figure 1 is 1500 MMf. (micro-microfarads), the value for one layer would be 6,000 times 1,500 which equals 9,000,000 MMf. In other words, the capacity of a plasma membrane 1 cm. square would be 9,000,000 MMf. Assuming a dielectric constant of 3 which is about the same as that of beeswax or cotton-seed oil, the thickness of the plasma membrane would be approximately 3 times 10^{-8} cm. which would be about 2 to 3 carbon atoms in thickness. Since the plasma membrane is probably impregnated with some water, its dielectric constant is probably greater than this, and if greater, it would be thicker. Fricke, on the assumption of a dielectric constant of 3, but obtaining a smaller value of the capacity, arrived at a value of 20 to 30 carbon atoms thick for the plasma membrane. We may conclude, therefore, that the plasma membrane is probably of molecular thickness. It is colloidal in the sense of being made of substances which are colloidal in solution and it is colloidal in the sense of having an extended surface for a small volume. It is probably not a smooth membrane but one made of molecules which are much branched. The membrane probably contains pores in between the branches of the molecules. The membrane substance probably has a specific resistance of 10^6 or about as great as serpentine. Owing to the fact that the membrane is of molecular thickness diffusion of Cl^- to equilibrium should take place rapidly and the difference in concentration between plasma and corpuscle is probably due to a Donnan effect.

From the conductivity measurements on laked blood, we may conclude that the corpuscle interior is about three times as resistant as the serum and therefore with equal mobilities of the ions the total ion concentration in the corpuscle might be considered only one-third the value of the serum. However, the corpuscle interior is very high in protein content, there being a higher hemoglobin concentration than

in a hemoglobin crystal, and this high protein content might cut down the speed of ions considerably. It therefore seems probable that the ionization in the corpuscles is greater than one-third the value in the serum.

The impedance of the intact corpuscle to a current of a million cycles per second seems to be twice as great as the resistance of the laked corpuscle. Since the corpuscles were laked without the addition of any water, there was no dilution of the proteins to account for an increase in conductivity. It is possible that a million cycles per second is not high enough frequency to reduce the impedance of the plasma membrane to a negligible value. We are working with higher frequencies but are not ready to report on any of these experiments.

In conclusion, these results support the contention of a colloidal semi-permeable membrane on the cell surface. This membrane is not semi-permeable to all substances. It has appreciable electric conductivity which may be accounted for by permeability to chlorine ions. These results are compatible with the views expressed by Warburg,²⁷ Van Slyke²⁸ and Henderson,²⁹ by whom it is assumed that the plasma membrane of the red blood cell is impermeable to potassium and sodium ions but permeable to Cl and HCO_3 ions. The Cl ion concentration according to Henderson, is about .75 as great in the corpuscle as in the serum. The same would be true of the HCO_3 ion concentration if we neglect the effect of the difference in potential between the inside and outside of plasma membrane. I am not sure whether we have any data whatever indicating the ionization of potassium inside the corpuscle.

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²⁷ *J. Biochem.*, **16**, 153 (1922).

²⁸ Van Slyke and McLean, *F. C. J. Biol. Chem.*, **56**, 765 (1923).

²⁹ Henderson, Bock, Field, and Stoddard, *J. Biol. Chem.*, **59**, 379 (1924).

THE FUNCTION OF CARBON MEMBRANES IN OSMOSIS

BY F. E. BARTELL AND H. J. OSTERHOFF

A subject concerning which there has been considerable disagreement and diversity of opinion is presented in the problem of the function of the membrane in the process of osmosis. One of the chief reasons for the disagreement is that the different theories proposed have been based upon quite different types of experimental results.

Most of the outstanding theories have been based upon results obtained with truly semi-permeable membranes, i.e., membranes which will permit the passage of solvent but not of solute. It has been proven experimentally that when a truly semi-permeable membrane (such as copper ferrocyanide in its relation to aqueous sugar solution and pure water) is used the magnitude of the pressure which is built up between the two sides of the membrane is determined by the properties of the solution and the solvent, that insofar as the magnitude of pressure is concerned, the function of the membrane need not be considered. It is admissible to state that such osmosis and resulting osmotic pressure is due to the difference in thermodynamic potential of pure solvent and solution. The pressure measured represents a tendency toward equalization of the thermodynamic potential. In order to define the thermodynamic environment of the solvent in the different parts of the liquid system, and in order to measure its escaping tendency, such factors as vapor pressures, surface tension, specific volume, heats of solution, etc., must be considered. Valuable as the thermodynamic theory of solutions has proven to be, it has, however, given us practically no information as to the actual mechanism of osmosis. Further, with our present limited knowledge of the properties of solutions, it can aid us practically not at all in predicting the osmotic force which may be expected in systems with membranes which are not truly semipermeable and with which we have capillary effects of unknown but considerable magnitudes. It is well known that osmotic flow can be obtained through membranes which are far from being strictly semi-permeable. In such systems fairly great osmotic forces are set up, and pressures of considerable magnitude are obtained, though "maximum osmotic pressure" values are never reached. In some cases we find that the operation of the osmotic force (and at least the initial direction of flow of liquid) is, in fact, opposite to that which apparently is demanded

by the thermodynamic potential of the liquid system. In such cases the membrane must surely play an active part. It is, then, not surprising that osmotic theories based upon experimental results obtained with such systems as these should be different from those theories which have been obtained from systems having truly semi-permeable membranes.

In the one case we are dealing with osmotic effects arising from a process in which equilibrium conditions can be obtained. A system of this type is obviously capable of thermodynamic treatment. In the other case, we are dealing with a process in which (owing to diffusion through the membrane) equilibrium conditions are not obtained. Capillary forces influence the magnitude of the measured pressures, and the customary thermodynamic reasoning cannot be applied.

Semi-permeability:

Before we can determine definitely the function of an osmotic membrane we must first study the nature of semi-permeability. Many theories have been offered to account for the mechanism of semi-permeability. According to Traube¹ a semi-permeable membrane functions as an "atomic sieve," permitting solvent molecules to pass while restraining solute molecules. Various theories such as the kinetic theory find this view sufficient. Likewise, from the standpoint of thermodynamic treatment no further concept is necessary. Supporters of the so-called solution theory, L'Hermite,² Overton,³ and others have held that a strictly semi-permeable membrane is one permeable only to substances which will dissolve in it. A slight modification of this theory, namely, that the permeability of a membrane is due to its absorptive or adsorptive power for different substances has been supported by Liebig,⁴ Nernst,⁵ Kahlenberg,⁶ Flusin⁷ and others.

Armstrong⁸ has gone still further and has postulated chemical interaction between the membrane and the substance diffusing through it. The various theories presented range, in fact, from the concept of diffusion through capillary pores which serve as molecular filters to the concept of intra-molecular penetration or chemical reaction. Both I. Traube⁹ and Bigelow¹⁰ have attempted to reconcile these views, the latter suggesting that there really is no sharp demarkation between

¹ *Archiv für Anat. Physiol., und Wissensch. Med.*, 87 (1867).

² *Ann. chim. phys.*, 3, 43, 420 (1855).

³ *Z. physik. Chem.*, 22, 189 (1897).

⁴ *Liebig's Ann.*, 121, 78 (1862).

⁵ *Z. phys. Chem.*, 6, 35 (1890).

⁶ *J. phys. Chem.*, 10, 141 (1906).

⁷ *Ann. chim. phys.*, (8), 13, 480 (1908).

⁸ *Proc. Roy. Soc.*, B81, 94 (1909).

⁹ *Phil. Mag.*, (6), 8, 704 (1904).

¹⁰ *J. Amer. Chem. Soc.*, 29, 1675 (1907).

capillary phenomena and the process of solution on the one hand, and the process of solution and of chemical reaction on the other; that "the phenomena of chemical affinity seem to merge, without any abrupt change, into capillary phenomena." This view appears to be justified and its acceptance goes far toward harmonizing the results obtained by different experimenters. Bancroft¹¹ attempted to harmonize these views by assuming that "we can have two types of semi-permeable membrane, one with a continuous film and the other with a porous one. In the case of a continuous film, it is essential that the solvent shall dissolve in the membrane and that the solute does not. With a porous film we shall have a semi-permeable membrane only in case we have strong negative adsorption—adsorption of the solvent and not of the solute—and in case the diameter of the pores is so small that the adsorbed liquid fills the pores completely leaving no central channel through which the solution can diffuse." This view, while not radically different from the one previously stated insofar as the property of semi-permeability is concerned, does make it possible for us to obtain a somewhat better concept of the mechanism of the osmotic process. According to this view, a given osmotic membrane might function as a semi-permeable membrane in one system and not so function in another system, the semi-permeability depending upon the degree of selective adsorption by the membrane of the components of the liquid system. Tinker¹² has made a study of "semi-permeable" copper ferrocyanide membranes and has concluded that pores of measurable diameters do exist.

Work of Other Investigators:

Many investigators have worked with osmotic systems in which two liquids such as alcohol (ethyl or propyl) and water have been used. The results obtained have been so inconsistent that they have led to a diversity of conclusions.

Pickering¹³ describing the experiments in which he used propyl alcohol and water with an unglazed porcelain vessel stated that when the alcohol and water were put in the semi-permeable vessel and placed in water the latter passed inward toward the solution, the vessel appearing to be permeable to water but not to the alcohol. When this same vessel with its contents was placed in propyl alcohol, the alcohol passed inward toward the solution, the vessel now appearing to be permeable to the alcohol. He concluded that "it is the solution and not

¹¹ Colloid Symposium Monograph, 3, 17 (1925).

¹² *Proc. Roy. Soc.*, 92, 357 (1916 A).

¹³ *Ber.*, 24, 3689 (1891); *Nature*, 55, 224 (1897).

either of the substances separately, to which the membrane is impermeable." He believed this experiment tended to substantiate the hydrate theory of osmosis, "the molecules of hydrates being necessarily larger than those of their constituents." Findlay and Short¹⁴ tried later to duplicate Pickering's results, but failed. They have pointed out that the conditions under which they worked might not have been the same as those under which Pickering worked. They stated, however, that it is difficult to find a theoretical basis for the possibility of such results as he obtained. Barlow¹⁵ criticizing the work of Pickering states that "the observation of an increase in osmotic pressure after the cell had been placed in alcohol is correct, but that it is not due to an inflow of the alcohol" (but in reality is due to inflow of water already within the cell pores). "Had more time been given to the experiment, it would have been found that this increase is not as permanent as when the cell is immersed in water. The permanent result is an outflow from the cell into the alcohol."¹⁶

Barlow performed an experiment in which pure water within a cell was separated from alcohol by a guttapercha membrane—alcohol flowed inward to the water. In another experiment, alcohol in a cell was separated from water by a copper ferrocyanide membrane. In this case water flowed inward to the alcohol. He concludes from the results of his own experiments and from the results of others that "the cause of the current is the same in each case, namely, the mutual potential energy of the liquids; the direction of current is conditioned by the membrane." He also states: "In any adequate theory of osmotic pressure, the part played by the membrane must be taken into account. This necessary part is that the membrane must absorb that liquid which in going through forms the osmotic current. Nernst,¹⁷ Flusin,¹⁸ Kahlenberg,¹⁹ and others have expressed similar views. Flusin²⁰ carried out an experiment in which water and alcohol were separated by a bladder membrane. The flow was from water to alcohol. Kahlenberg²¹ separated water and alcohol by rubber; the flow was from alcohol to water.

The following table gives the type of osmosis obtained with different organic liquids against water.

¹⁴ *Trans. Chem. Soc.*, 87 (1905).

¹⁵ *Phil. Mag.* (6), 10, 1 (1905).

¹⁶ Barlow's detailed explanation as to the cause of the initial flow and subsequent reversal will not be taken up in this paper, inasmuch as Barlow assumed the existence of a copper ferrocyanide membrane within the walls of the porcelain. Findlay (*loc. cit.*) has given us the information that Pickering informed him in a private communication that a porcelain cell with no precipitated membrane within it was used.

¹⁷ *Loc. cit.*

¹⁸ *Compt. rend.*, 131, 1308 (1900).

¹⁹ *J. phys. Chem.*, 10, 141 (1906).

²⁰ *Loc. cit.*

²¹ *Loc. cit.*

Liquid No. 1	Membrane	Liquid No. 2	Direction of Flow	Observer
Water	bladder	alcohol	—————→	Flusin
Water	rubber	alcohol	—————←	Kahlenberg-Barlow
Water	copper-ferrocyanide	alcohol	—————→	Barlow
Water	nickel-ferrocyanide	alcohol	—————→	Battelli-Steffanini ²²
Water	rubber	pyridin	—————←	Kahlenberg
Water	parchment	pyridin	—————→	Kahlenberg

From the foregoing experiments a logical conclusion is that the nature of the membrane is largely responsible for the direction of osmotic flow, that the liquid which is most highly adsorbed by the membrane (i.e., the liquid which has the higher wetting power for the membrane or is imbibed to the greater extent) is the liquid which will pass through the membrane giving the osmotic current.

When two pure liquids are separated by a semi-permeable or very nearly semi-permeable membrane the nature of the membrane does undoubtedly determine the direction of flow. But when the membrane is not strictly semi-permeable, the properties of the liquid system may be the deciding factor. If this view is correct, the permeability or pore size of the membrane is an important factor in deciding the nature of osmotic effects. We believe, then, that in the study of an osmotic system the three factors (1) properties of the liquid system, (2) relative adsorption of liquids by the membrane, and (3) pore size, must all be considered, the results obtained being dependent upon the interrelationship of these three factors. Let us take the following examples:

(a) In case the membrane be one with exceedingly fine pores and in case but one component is adsorbed, the pore spaces will be filled only with the liquid adsorbed and the flow of this liquid will occur so as to satisfy the thermodynamic potential of the liquid system and "maximum osmotic pressure" values will be obtained.

(b) In case the pore diameter of the membrane is somewhat greater than in (a) and not truly semi-permeable, relative adsorption effects will play an important part and even though the system may consist of two miscible liquids the liquid within the pore space may be almost entirely that liquid which is most highly adsorbed. Under these conditions, flow through the membrane will tend to be from that liquid which is most highly adsorbed. On the other hand, forces resulting from the thermodynamic potential of the liquid system might, however, be the factors deciding direction of flow. Under these conditions the direction

²² *J. de Phys.*, 6, 402 (1907).

of liquid flow might not be from that liquid which is most highly adsorbed. In this case (b), then, we may state that osmosis might result, an osmotic flow might be noted, pressures might be developed and measured, but "maximum osmotic pressure" values would not be obtained. Moreover, neither the magnitude of the pressures developed nor even the initial direction of flow of the liquid can be definitely predicted.

(c) In case the pore diameter of the membrane be so great that both components of a binary system can diffuse through with but limited restraint, the direction of flow of liquid will be largely dependent upon the properties of the liquid system and not dependent upon the nature of the membrane.

It is obvious that when pore diameters are too great no osmotic effects will be obtained. It has been shown that the appearance of osmose is, to a certain extent at least, dependent upon the pore size of the membrane.²³

It has been found that osmotic effects can be obtained with unglazed porcelain membranes when the pores are so clogged with different materials that the largest pores have diameters not greater than about 0.5 micron. Distinct osmotic effects have been obtained with membranes of collodion in which the largest pores had diameters as great as 1.6 microns. Osmotic flow has been observed with membranes of such inert materials as unglazed porcelain²⁴ and compressed gold, platinum, carbon, and silica.²⁵ Such membranes surely had capillary spaces through them and it was found that when such pore spaces have a diameter of not more than about 0.5 micron osmotic effects may be obtained. With such membranes both components of a binary system (i.e., both solute and solvent) can pass through the pores. With such membrane systems the rate and even the initial direction of osmotic flow is dependent largely upon the properties of the membrane.

From the foregoing discussion, it appears one should be able by altering the pore diameter of the membrane to alter greatly the nature of the osmotic effects. By employing membranes of a given material, and using certain liquids, one should be able to obtain osmotic forces operating in one direction with membranes with large pores and then osmotic forces operating in the other direction with membranes with fine pores. It should be possible to prepare a membrane of a finely divided substance such that when loosely packed it would give an osmotic tendency in one direction, while when tightly packed it would give an osmotic tendency in the other direction. Such effects have actually been obtained in our work.

²³ Bigelow and Bartell, *J. Amer. Chem. Soc.*, **31**, 1194 (1909); Bartell, *J. Phys. Chem.*, **15**, 659 (1911).

²⁴ Graham, *Phil. Trans.*, **144**, 177 (1854); Bigelow and Bartell, *loc. cit.*

²⁵ Bigelow and Robinson, *J. Phys. Chem.*, **22**, 99, 158 (1918).

The Present Investigation:

In the present investigation membranes were prepared by compressing finely divided silica or carbon, substances which are relatively inert chemically. Silica prepared by different methods was ground to 350 mesh or finer. Different kinds of carbon, as sugar charcoal, commercial activated chars, and lamp black were used and were found to give comparable results. In the experiments described below a good grade of lamp black thoroughly extracted with ether was used. Membranes were prepared by compressing the silica or carbon in cells between

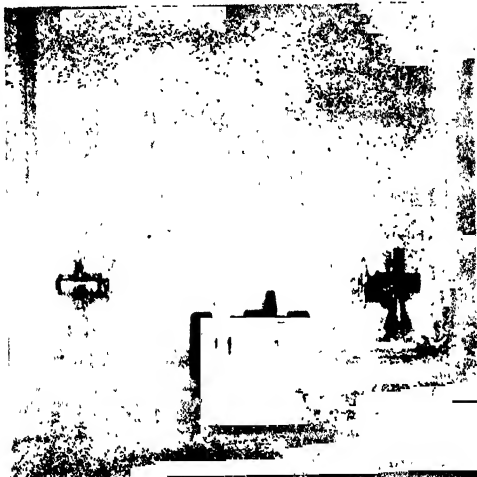


FIG. 1.

perforated metal discs by means of an hydraulic press. Pressures in different experiments ranged from approximately 2500 to 20,000 pounds per square inch. With the lower pressures the largest pores probably had diameters not greater than about 0.5 micron.

The cells were of special design as illustrated in Figure 1. The volume of each cell chamber was approximately 25 cc. Temperature = approximately 25° C.

The results given in the following table are qualitative rather than quantitative but tend to show the direction of osmotic flow. Something of the magnitude of the osmotic force will be indicated by the data which show the difference in level of the liquid columns of the two cells. Inasmuch as qualitative data only was desired at this time no attempt was made to obtain a quantitative relationship of pressures developed by the different systems.

RESULTS WITH SILICA MEMBRANE

Compartment No. I	Liquid in Membrane	Compartment No. II	Direction of Flow	Time Hours	Difference in Liquid Levels in Cm.
Compressed at approx. 10,000 lbs./sq. in.					
Water	Water	Ethyl alcohol	————→	3	20
Water	Water	Propyl alcohol	————→	3	16
Water	Water	" " 55%	————→	3	12
Water	Water	" " 35%	————→	3	8
Water	Water	" " 17%	————→	3	5
Water	Water	Acetone	————→	3	28
Water	Water	Amyl alcohol	————→	3	10
Water	Amyl alcohol	Amyl alcohol	————→	3	25
Water	Water	Pyridin	————→	3	10
Water	Water	Sugar solution 4%	————→	3	12

RESULTS WITH CARBON MEMBRANES

Compartment No. I	Liquid in Membrane	Compartment No. II	Direction of Flow	Time Hours	Difference in Liquid Levels in Cm.
Pressure of compression = approx. 10,000 lbs./sq. in.					
1. W	A	A	————→	3	36.6
2. W	W	A	————→	3	29.9
3. W	W	50% A.W	————→	3	14.7
4. W	50% A.W	50% A.W	————→	3	10.0
5. 50 A.W	A	A	————→	3	6.5
6. 50 A.W	50 A.W	A	————→	3	5.8

Pressure of compression = approx. 10,000 lbs./sq. in.

Acetone — Water					
1. W	Ac	Ac	————→	3	43.0
2. W	W	Ac	————→	3	28.5
3. W	W	50 Ac.W	————→	3	22.0
4. 50 Ac.W	Ac	Ac	————→	3	11.2
5. 50 Ac.W	50 Ac.W	Ac	————→	3	14.0

Pressure of compression = approx. 20,000 lbs./sq. in.

Pyridin — Water					
1. W	P	P	————→	3	11.5
2. W	W	P	————→	2	— 10
			————→	3	— 11
			————→	6	— 4
			————→	17	+ 22.7
3. W	W	50 P.W	————→	3	9.1
4. W	50 P.W.	50 P.W.	————→	3	4.0
5. 50 P.W.	P	P	————→	3	21.8
6. 50 P.W.	50 P.W.	P	————→	3	1.6
Water-sugar soln					
W	W	Sugar soln	————→	3	> 3

* The symbol W indicates water; A, alcohol; Ac, acetone; P, pyridin; 50 A.W = 50 per cent mixture of alcohol and water, etc. W membrane indicates that initially the membrane pores were filled with water, in fact all the finely divided material used was wetted by liquid before compression. The arrow indicates direction of osmotic flow.

We are indebted to Mr. C. N. Smith and Mr. Ying Fu of this laboratory for assistance in obtaining the experimental data with osmotic cells with carbon and silica membranes.

The results show that with the Silica membrane systems the direction of flow was in all cases from water to the organic liquid. This is what we would expect in case relative adsorption is the deciding factor in determining the direction of flow.

With the carbon membrane systems the direction of flow was eventually at least, from water to the organic liquid. This is not what we would expect in case flow is from the liquid which is most highly adsorbed by the membrane.

With water and alcohol the flow was in all cases toward the alcohol. Likewise with water and acetone the flow was toward the acetone. In the case of pyridin with carbon membranes the initial effects were somewhat different; with the system Water-Water-Pyridin the flow was first from pyridin to water then later from water to pyridin (results were similar but different in magnitude with compression pressures of 10000# and 20000#). We might reason from this experiment that the initial effect was due to displacement of water by pyridin owing to the greater adsorption of pyridin by carbon. Then when the membrane pores became filled with pyridin the flow was toward that liquid in which there is the greater affinity or liberation of free energy, i.e., the thermodynamic potential effects predominate. The mechanism of osmose at this point is admittedly difficult to understand.

It appears that the thermodynamic properties of these systems are such that in so far as the liquids are concerned the tendency for flow is from water to the organic liquid. It appears, however, that in some cases at least the properties associated with the membrane (i.e., the capillary effect) are such as to alter or even reverse this normal direction of flow. Other experiments described below will show the correctness of this view. It was found that with membranes compressed at approximately 5000# the flow pyridin to water was slight, less than 1 cm. liquid pressure, and reversal occurred within 2 hours, after which pressures of as much as 29 cm. liquid were obtained after 24 hrs. With membranes compressed more highly the initial flow of pyridin to water was greater and reversal occurred after a longer period of time.

It was to be expected that the organic liquids would be more highly absorbed by carbon than is water. Preliminary tests made with an interferometer confirmed this view. From the theory that the direction of flow should be from that liquid which is the more highly absorbed we would expect the flow to be from alcohol to water—the flow actually was in the other direction.

A series of tests were undertaken to show whether it can be proven experimentally that organic liquid will actually displace water from carbon. By making use of an apparatus we were using in a study of relative wettability and relative displacing effects of one liquid by another, we were able to throw light on this problem.

Displacement of One Liquid by Another from a Finely Divided Solid.

Cells of the type illustrated were used. Figs. 2-3. These cells were so constructed that one half of the chamber could be filled with finely divided solid (carbon) wetted with one liquid and the other half filled with finely divided solid (carbon) wetted with another liquid, the two

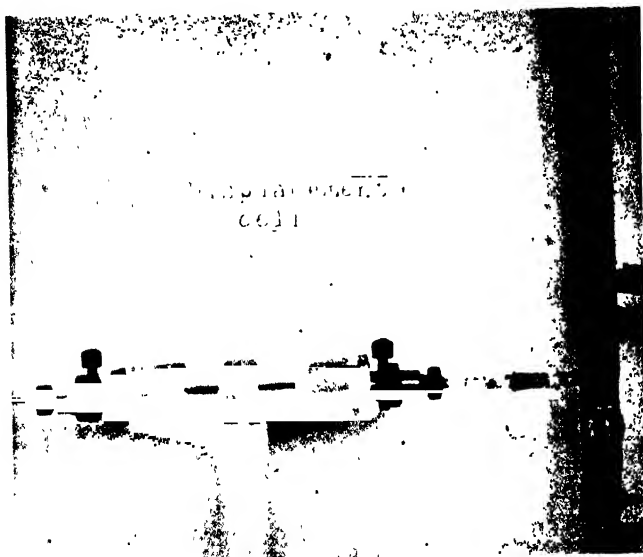


FIG. 2.

compressed masses being in contact with each other and with the corresponding liquids in the two cell compartments. It is well known that in similar systems in which two immiscible liquids are used the liquid with the higher wetting power for the solid will displace the other liquid. Water, for example, will displace oil from the capillary pores of fine sand. So far as we are aware there is no data in the literature which shows that in the case of two completely miscible liquids one of the liquids will displace the other liquid from finely divided solid and in so doing expel it from the system, i.e., drive it out, producing thereby a flow of the less readily adsorbed liquid from the system through

which action displacement forces of considerable magnitude may be set up.*

By opposing the movement of liquid and by noting the pressures required to balance the displacement forces we obtained what we believe to be a partial measure at least of the relative wetting power of the different liquids for a given solid. The result of this work will be given more fully in another paper.

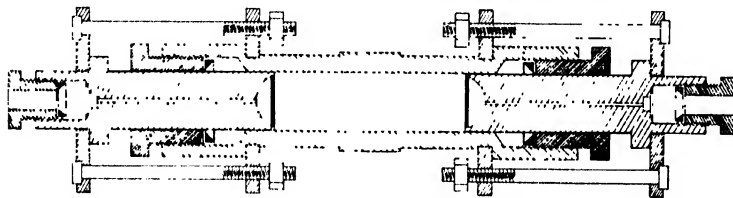


FIG. 3.

We have found that when the packing of carbon (or other finely divided substances) is sufficient, i.e., when the capillary spaces have become sufficiently small, two miscible liquids may be opposed as above described and that liquid with the greater wetting power will displace the other liquid with sufficient force to build up considerable pressure.

The following tables will give some of the results obtained.

Compartment No. 1	Solid Compressed	Compartment No. 2	Direction of Flow	Pressure
Pressure of compression 2500 lb/sq. in. (approx.).				
Water	Carbon	Toluene	←	2670 mm Hg.
Water	"	C C l ₄	←	2840 " "
Water	"	Pyridin	←	750 " H ₂ O
Water	"	Acetone	←	295 " "
Water	"	Propyl alcohol	←	192 " "
Water	"	Ethyl alcohol	←	180 " "
Water	Silica	Toluene	→	1360 " "
Water	"	C C l ₄	→	2210 " "
Water	"	Pyridin	→	15 " "
Water	"	Propyl alcohol	→	16 " "
Toluene	Carbon	C C l ₄	←	193 " "
Pyridin	"	"	←	" "
Propyl alcohol	"	"	←	" "
"	"	Toluene	←	386 " "
"	"	Pyridin	←	139 " "
"	"	"	←	566 " "

Active flow of liquid was opposed by building up sufficient pressure on the positive pressure side of the system. Thick membranes (about

* Since the presentation of this paper we have found one case mentioned in the literature of displacement of one liquid by another miscible with it. Brucke (*Pogg. Ann.* **58**, 77-94, 1843) observed that in a very narrow glass capillary pure turpentine displaced olive oil. At the end of 24 hours he measured a displacement of 0.6 mm. He was unsuccessful in his attempts to obtain displacement in the other two miscible liquid systems, although he considered that theoretically such displacement might be possible.

2 inches thick) were used so that the pores were of sufficient length to prevent movement of the liquid-liquid interface to the membrane face during the setting up of the cell and before the external pressure could be applied and measured. From the above data it will be noted that when such thick carbon membranes are used and when the pore size is sufficiently reduced osmotic forces are set up and movement of liquid tends to be from that liquid which has the greater wetting power for the membrane.

It was further found that by altering the degree of packing and pore size we could alter the magnitude of the effects. When the pores were too large there was no apparent flow of liquid through the membrane.

It is felt that this experimental work is sufficient to substantiate the view that the three factors (1) thermodynamic potential of the liquid system, (2) relative adsorption of the components of a liquid system by the membrane, and (3) pore diameter of the membrane must all be taken into consideration in a study of osmotic effects produced in a system in which the membrane used is not strictly semi-permeable. A more quantitative study along this line is under way and quantitative data will soon be available.

Conclusions:

1. When we have a strictly semi-permeable membrane separating two pure liquids we are dealing with a system in which one component is adsorbed with the practical exclusion of the other. In such a system flow of liquid can be from that liquid only which is adsorbed by the membrane. This conclusion conforms with the generally accepted views.

2. With systems having a membrane with greater permeability, i.e., with fine pores but not strictly semi-permeable, the initial osmotic force and resulting direction of flow of liquids will be determined largely by the relative adsorption of the liquids by the membrane material. In such cases the membrane does play an active part and the capillary effect is a deciding factor in determining the initial direction of flow.

3. When a fairly permeable and sufficiently thin membrane is used the osmotic flow of solution in a binary liquid system will be dependent upon the properties of the liquid system. The properties of the membrane may not govern the direction of flow of liquid.

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ELECTROENDOSMOSE THROUGH WOOD MEMBRANES

BY ALFRED J. STAMM¹

The phenomenon of electroendosmose has in general been studied with one of two objects in view. The first has been to explain the mechanism of the phenomenon and to develop mathematical expressions showing its relationship to its determining factors. The second has been to determine such electrical properties of electrolytic solutions as transference numbers and degree of hydration of the ions. The present investigation was undertaken from a somewhat different viewpoint, namely that of determining the relationship of electroendosmotic phenomena to the known microscopic structure of the membrane material and the less understood extent of its colloidal dispersion.

Microscopic Structure of Wood:

Wood is a complex cellular material which shows definite structural differences in its three space directions, namely, transversely, radially, and tangentially. The chief cellular structure is laid down in the longitudinal plane of the tree. The cells vary in size, shape, and function, some serving primarily to conduct sap, others to store food, and still others to give strength to the tree. Some of the cells, differentiated as fibers, are long, narrow, tapering tubes closed at both ends. (See Figures 2 and 3.) Their length varies from about 0.03 to 1.0 cm. Scattered among the fibers of hardwoods are cells of a larger diameter which have open ends and are placed one above the other forming continuous tubes called pores or vessels. Some hardwoods have pores of fairly constant diameter rather uniformly dispersed throughout the wood. These are known as diffuse-porous woods. Other hardwoods have their larger pores in more or less concentric rows in the springwood with smaller pores in the denser summerwood of each annual layer of growth. These are known as ring-porous woods. In softwoods there are no pores, but there may be special intercellular spaces known as resin passages which serve to store and conduct resins.

The nature of the cells or fibers formed varies for the different parts of the growing season. The cells formed in the spring of the year are in general larger than those produced later in the year, and have considerably thinner walls. (See Figure 1.) A line of demarka-

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SITKA SPRUCE SECTIONS

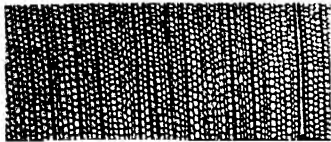


FIG. 1.—Transverse. $\times 25$.

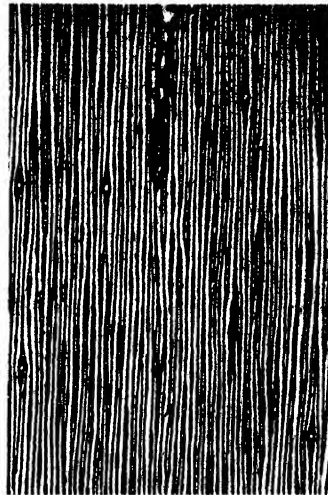
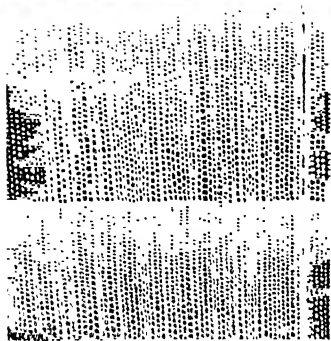


FIG. 2.—Tangential. $\times 25$.

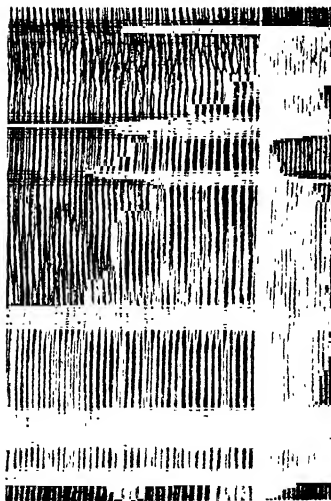


FIG. 3.—Radial. $\times 25$.



FIG. 4.—Transverse. $\times 975$.

tion results between the last wood formed in the summer and the new growth which commences again in the spring. One cycle of the resulting banding, the spring- and summerwood of the same year, is known as an annual ring. The distinctness of the line of demarkation between the summerwood and springwood of succeeding annual rings differs for the different kinds of wood and depends to a great extent upon the conditions of growth. In some cases, the rings are so narrow that they can hardly be observed with the naked eye. Then again the rings may be as much as 1.5 cm. across. The lines of demarkation between the summerwood and the springwood laid down the following year appear to be lines of weakness, at least in some species of wood. Ring shakes, that is small visible cracks, occasionally occur at these places. Mr. Bateman of the Forest Products Laboratory has obtained indications to the effect that similar invisible cracks may play a part in the drying of wood and the impregnation of preservatives in the tangential direction.

In practically all woods, there are groups of cells running in a radial direction in the tree trunk perpendicular to the fibers and across the annual rings. These are known as medullary rays. Their function is to store food and conduct sap from the bark to the sapwood, or living outer layer of wood in the growing tree. These rays are made up of a number of individual cells, the number varying considerably for different kinds of wood and even in the same piece of wood. (See Figure 2.) Radial resin passages occasionally occur in the rays.

It was mentioned that the fibers are closed at both ends. They communicate with each other, however, through thin portions of the cell wall known as pits. A face view of the pits can be seen on the longitudinal sections, chiefly the radial (Figure 3), and the manner of communication between the cells on a transverse section (Figure 4). The pits occur at adjacent partially unthickened points of the adjoining cell walls. They are spanned by a thin membrane, a continuation of the middle lamella between the cells, which particularly in the case of softwoods shows a slight central thickening called the torus. These membranes are often fairly permeable, and in some cases have been found to contain actual perforations, thus affording communication between cells.² Under special conditions of pressure the torus may close the pit orifice and present its greater thickness as an obstruction to the passage of liquids. There may also be obstructational growth within the pore or vessel cavities in the form of tyloses. Further, resin deposits may obstruct the resin ducts and ray cell passages.

The distribution of the chemical constituents throughout the wood substance, as far as is known, seems to be fairly uniform with the ex-

² Bailey, *Forest Quarterly*, XI, No. 1, 12 (1913); Am. Railway Engineering Association, Bull. 174 (1915).

ception of the middle lamella which has been shown by Ritter³ of the Forest Products Laboratory to be practically pure lignin. Further microchemical studies may, however, reveal other chemical differences.

Sections Studied.

Transverse, radial and tangential sections of five softwoods and one hardwood were studied, namely Sitka spruce, Alaska cedar, western red cedar, western hemlock, Douglas fir and yellow poplar. The latter hardwood belongs to the diffuse-porous group. All sections were taken from the heartwood of air dried stock. The sections varied in thickness from 0.4 to 2.0 mm. In the case of the transverse sections most of the cells were cut across twice so that a large portion of the cell cavities were completely open, thus giving an effective capillary cross section that approached the cross section of the cell cavities. The capillary cross section of the tangential sections was made up largely of the ray cell capillaries together with any slight cross grain capillarity of the resin ducts, pores, and fibers caused by a slight unavoidable deviation of part of the cell structure from parallelism with the membrane faces. This would be expected to be small in the case of the fibers as their length is considerably less than the distance across the membrane at a small angle with its surface. Undoubtedly the resin ducts and pores show a considerably greater effective capillarity. Besides these sources of capillarity there is the possibility of capillary communication from fiber cavity to fiber cavity through the pits which occur on the tangential faces of the fibers. Finally there is the possibility of a natural submicroscopic capillarity. The capillary cross section of the radial sections may be made up of all the above factors with the exception of the ray cell capillarity. There might also be an additional ring shake capillarity.

All of these sections were soaked in distilled water or 95 per cent alcohol for two weeks. To facilitate the replacement of air by water or alcohol, the soaking of the sections was done in a vacuum desiccator to which intermittent suction was applied. The alcohol was thoroughly washed out with distilled water from the alcohol soaked sections before they were used in the electroendosmose experiments.

Apparatus.

The apparatus used in this investigation was the modified Brigg's apparatus⁴ used by Strickler and Mathews⁵ in their studies of the electroendosmose of non-aqueous solutions (Figure 5). A potential of 1080 volts (24 "B" batteries 45 volt) was applied between the electrodes

³ *J. Ind. Eng. Chem.*, **17**, 1194 (1925).

⁴ Briggs, *J. phys. Chem.*, **22**, 256 (1918).

⁵ Strickler and Mathews, *J. Am. Chem. Soc.*, **44**, 1647 (1922).

E. The resulting drop in potential across the membrane M caused a motion of the liquid from anode to cathode thus causing the motion of the bubble B in the capillary tube. This motion was recorded in cubic centimeters per second. The membrane cross section was 7.76 cm^2 and the distance between the platinum coil electrodes was 6.5 cm . Three capillary bubble tubes were used with cross sections of 0.0251 cm^2 , 0.0550 cm^2 and 0.0909 cm^2 . Check values for the velocity were obtained with the different capillaries except in cases where the velocity

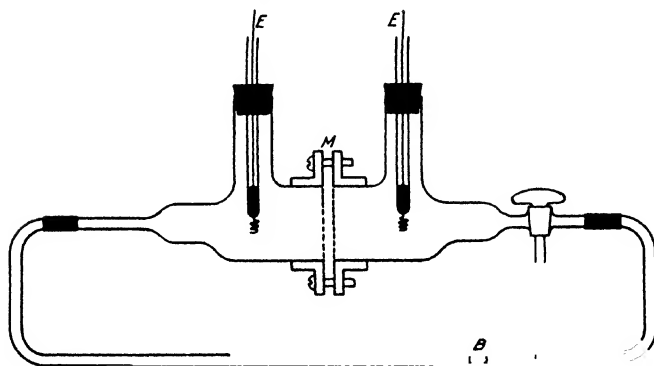


Fig. 5. Electroendosmose Apparatus.

was so great that an appreciable pressure was built up in the electrode tubes which could not be immediately dissipated in moving the bubble. This was apparent from an appreciable motion of the bubble after breaking the electrical circuit. For this reason, the larger capillary tube was used for membranes of high porosity which gave high values for the rate of flow of the liquid. The length of the bubble used (1.5-2.0 times the diameter) did not affect the rate. The apparatus was immersed in a thermostat held at $25^\circ \text{ C.} \pm 0.05$. Slight fluctuations in the temperature had but a very small effect on the rate. The rate of motion of the bubble built up slightly upon closing the electrical circuit so that the rates were determined after the velocity of motion of the bubble became constant.

The drop in potential across the membranes was measured with a potentiometer. Platinum black foil electrodes were held securely up against the faces of the membranes and these were connected in series with 99,000 ohms resistance. The potential drop across 2,000 ohms of the resistance was read on the potentiometer. The high resistance shunt caused but a slight reduction of the current passing through the membrane. Reversible calomel electrodes and agar connections to the

membrane, as described by Fairbrother and Mastin⁶ were tried. The results checked within one per cent the values obtained by the above method. As the first method was simpler in manipulation, it was used almost exclusively. A milliammeter was placed in the applied voltage circuit. With no membrane in the cell a current of approximately 7.0 milliamperes was obtained with the distilled water used (P₁₁ 5.1-5.6). Deviations from this value for the different samples of distilled water used were applied as a correction to the measured potential drop across the membranes so as to put all the values on a comparable basis.

Experimental Results.

In all cases studied, the direction of motion of the liquid through the membrane was from the anode to the cathode, indicating that wood has a negative charge with respect to water. Alkalies tend to increase the negative charge and acids decrease it. As far as the study has been conducted, no reversal of charge has been obtained. This is in agreement with some qualitative experiments by Bethe and Toropoff⁷ who tried wood membranes and Perrin's⁸ and Harrison's⁹ experiments using cotton cellulose. A further discussion of the effect of electrolytes on the electroendosmose through wood membranes will be reserved for another paper.

Some preliminary experiments were made to test the validity of the electroendosmose equations,

$$P = (300)^2 \frac{4\pi\eta V}{EDq} = (300)^2 \frac{4\pi\eta V L^-}{ID}$$

where P is the contact potential between the adsorbed surface layer and the bulk of the liquid in volts, η the viscosity of the liquid, V the rate of endosmotic flow in cc. per second, L^- the specific conductivity of the liquid in the membrane, E the potential gradient through the membrane in volts per cm, I the current flow in amperes, D the dielectric constant of the liquid, and q the total capillary cross section of the membrane. The linear relationships between the rate of flow V and the potential E was found to hold over the whole range tested (270-1080 volts applied voltage) giving a straight line through the origin. Further a linear relationship was found to hold between V and q .

The membrane cross section $\frac{q}{x}$ was varied by using brass disk masks coated with shellac. (x is the fraction part of the membrane cross section made up of capillaries.) (Table I.)

⁶ *J. Chem. Soc.*, 125, 2319 (1924).

⁷ *Z. physik. Chem.*, 89, 597 (1915).

⁸ *J. chim. phys.*, 2, 801 (1904).

⁹ *Trans. Faraday Soc.*, 16, 116 (1920).

TABLE I
CHANGE IN VELOCITY OF FLOW WITH CHANGES IN MEMBRANE CROSS SECTION

Western Red Cedar, Transverse Section, Thickness 0.208 cm.

V cc. per sec.	$\frac{q}{x}$ cm.	$\frac{Vx}{q}$
0.0647.....	7.76	0.00833
.0413.....	5.11	0.00809
.0171.....	2.09	0.00818

E was but slightly affected by masking the membrane as the change in the resistance of the membrane was small in comparison with the total resistance, thus changing I but slightly. Slight variations in x due to the ununiform structure of the membranes can well account for the deviations in the above ratio.

TABLE II

Membrane	Sections	Thickness cm	I' cc. per sec.	E Volts per cm.	Remarks
Sitka Spruce	Trans.	0.157	0.0693	—	density
	"	.117	.0712	—	0.304
	"	.109	.0552	107.3	density
	"	.150	.0563	110.3	density
	Tang.	0.061	0.00453	272	} 0.408
	"	.056	.00424	275	
	"	.053	.00365	—	
Alaska Cedar	"	.043	.00575	—	slight check visible
	Rad.	0.117	0.000325	260	}
	"	.114	.000348	254	
	Trans.	0.137	0.0572	108.7	}
	"	.117	.0587	—	
	"	.186	.0547	107.1	
	"	.135	.0572	—	}
	Tang.	0.043	0.00148	241	
Western Red Cedar	"	.048	.00137	245	}
	Rad.	0.119	0.00023	222	
	Trans.	0.152	0.0676	106.0	} soaked in alcohol
	"	.208	.0676	106.8	
	"	.259	.0660	105.3	
	Tang.	0.076	0.00080	224	}
	"	.048	.00090	227	
Western Hemlock	Rad.	0.054	0.00021	215	}
	"	0.089	.00023	218	
	Trans.	0.139	0.0704	115.7	av. of 3
Douglas Fir	Tang.	0.071	0.00152	260	av. of 2
	Trans.	0.112	0.0546	118.3	av. of 2
Yellow Poplar	Tang.	0.087	0.00051	240	av. of 2
	Trans.	0.114	0.0176	112.2	av. of 3
	Tang.	0.068	0.00127	268	av. of 2
	Rad.	0.061	0.00048	262	av. of 2

Brackets indicate adjacent sections.

The velocities of electroendosmose and the potential gradients across the membranes studied are given in Table II. Good checks were obtained for the rates of endosmose through adjacent sections cut from the same piece of wood. Sections that were first soaked in alcohol gave similar values to the water soaked sections. This indicates that the alcohol had no effect on the nature of the membrane, and that a removal of the alcohol soluble resins had an inappreciable effect on the contact potential. Sections taken from the same kind of wood having different densities gave different velocities as shown by the data for Sitka spruce. The thickness of the sections seems to have but a slight effect on the rate for the thin sections used. When the thickness is increased appreciably, however, the rate of endosmose decreases due to a decrease in the proportion of capillaries that extend over the entire thickness of the membrane. The exact nature of this change in rate with thickness, and the influence of the bordered pits has been reserved for further study. The rate of endosmose is 10 to 100 times as great through the transverse sections as through the tangential sections, and 3 to 10 times as great through the tangential sections as through the radial.

The fall in potential across similar sections of the same kind of wood was found to vary directly with the thickness, that is, the potential gradient across the sections was constant. This gradient did not vary to any great extent from one species to another, but it did differ for the different types of sections. In general the ratio for the transverse to tangential to radial sections is as 1.0:2.3:2.0. As the current is constant, this ratio also represents that of the resistances. Similar ratios of the electrical resistance of wood in the three different space directions were obtained by Hiruma¹⁰ in measurements on wood containing approximately 15 per cent moisture. If the electrical conductivity of the sections studied in this investigation were the conductivity of the bulk water in the cell cavities and other large capillaries, the transverse section conductivity would be several thousand times that in the other two directions because of the exceedingly low conductivity of wood substance. As it is only about twice that in the other two directions in this case as well as in wood containing only 15 per cent water which is held in the fine colloidal structure, it seems quite conclusive that the conductivity is a surface phenomenon. Further evidence of this is obtained from the fact that the specific conductivity of water in the membrane is greater than that of water in bulk. The specific conductivity of the water used was 5.43×10^{-6} mho and that of an average transverse section 8.27×10^{-6} mho. On a water volume basis rather than a wood-water basis, the conductivity would be two to three times higher. The conductivity of water in wood is thus at least two to

¹⁰ *Extracts Bull. of Forest Exp. Station, Meguro, Tokyo.*

three times that of water in bulk. Such an increase in conductivity of water and of dilute solutions has been observed by Stock¹¹ in powdered quartz, and by McBain¹² in silica capillaries. It is believed to be due to the greater conductivity of the Helmholtz¹³ double layer.

Because of this increased conductivity of the liquid in the membrane, the contact potential can be calculated only when q is known, for q is not only involved directly in the first form of the equation but indirectly in the determination of l in the second form. Fairbrother

and Mastin¹⁴ have determined $\frac{q}{l}$ by conductivity measurements of

salt solutions of a sufficiently high concentration so that the specific conductivities of the solutions in bulk and in the membrane were the same. This may be satisfactory in the case of carborundum powders where there are no structural differences in the three space directions, and all of the liquid is of such a state of dispersion as to give electroendosmotic motion. This is not necessarily the case for wood membranes where part of the water may be held perhaps in a molecular dispersion. For this reason a different method of determining both q and p was tried.

A number of small holes varying in diameter from 0.044 cm. to 0.0913 cm. were drilled in the soaked tangential and radial sections, and the increase in the rate of electroendosmose was determined for the increase in q . The increase in rate of endosmose ΔV was found to be proportional to the increase in capillary cross section Δq over the range studied regardless of the size of the holes. Further, measurements showed no detectable change in E after drilling the holes. It hence seems justifiable to set up the equation:

$$P = (300)^2 \frac{4 \pi \eta}{E D} \frac{\Delta v}{\Delta q}$$

Table III gives the values of Δq and ΔV for different sized holes, and the values of the calculated contact potential. The contact potential varies but slightly among the species studied. The accuracy of the value of the contact potential is perhaps no better than 10 per cent even though many of the checks are much better than this. There is the possibility of distortion of the holes due to the release of existing stresses in the sections. This effect should not be great, however, in the saturated sections. A slight tearing effect on drilling, which is unavoidable, would also tend to give divergent values of Δq . The potential of wood against water is quite similar to the value obtained by

¹¹ *Anzeiger Akad. Wiss. Krakau*, A 635 (1912).

¹² *Trans. Faraday Soc.*, 16, 133 (1931).

¹³ *Wied. Ann.*, 7, 337 (1879); Freundlich, "Kapillarchemie," 221 (1920).

¹⁴ *Loc. cit.*

TABLE III

Membrane	Sections	Diameter of Holes in cm.	Δq cm. ²	ΔP cc. per sec.	$\frac{E}{P}$ Volts per cm.	P in volts
Yellow Poplar	Tang.	0.0610	0.0732	0.00216	273	0.0135
	"	* .0610	.0732	.00211	—	.0133
	"	.0610	.0732	.00202	263	.0132
	"	* .0913	.1630	.00459	—	.0134
	Rad.	.0610	.1464	.00424	262	.0138
	"	.0775	.2350	.00665	259	.0136
Alaska Cedar	Tang.	.0444	.1085	.00272	224	.0140
	"	.0520	.1482	.00350	—	.0132
	"	.0648	.1650	.00392	—	.0133
	"	.0780	.2390	.00562	—	.0131
	Rad.	.0610	.1464	.00358	222	.0138
	Tang.	.0635	.1580	.00380	224	.0134
Sitka Spruce	Rad.	.0635	.1580	.00387	215	.0142
	Tang.	.0635	.0790	.00235	273	.0136
	Rad.	.0635	.1580	.00478	263	.0144
Western Hemlock	Tang.	.0610	.1464	.00418	264	.0134
Douglas Fir	Tang.	.0610	.1464	.00366	237	.0132

* Additional increase in holes in the membrane given above

Harrison¹⁵ for the potential of cotton cellulose against water by streaming potential measurements. Harrison gives 0.0157 volt for the value against distilled water.

Having determined the value of P , the original value of q for each of the membranes can be calculated from the first equation. The percentage capillary cross section ($100 X$) is given in Table IV for the different sections. The per cent of total ray cell capillary cross section making up the total tangential cross section was determined from photomicrographs made with the assistance of Dr. Weinstein of the Forest Products Laboratory. The cross sections of the ray cells were cut out on the line of demarkation of the inner capillary wall from 20x16 inch enlargements (250 times). These were weighed, and the weight was divided by the total weight of the photomicrograph prints. These values are given in the last column of Table IV. They check quite well with the capillary cross sections obtained from the electroendosmose measurements, thus indicating that the submicroscopic capillarity, pit communication capillarity, and cross grain capillarity are all very small in comparison with that of the ray cells. The results from the two different methods of measuring the capillarity differ appreciably only in the case of yellow poplar. The original photomicrographs indicated a rather large deviation in the distribution of the ray cells for poplar which was not the case for the softwoods. The two values given were from enlargements taken from different parts of the same photomicrograph, whereas the two values for Sitka spruce were from entirely different specimens of different density. The ray cells of the poplar are further quite short and subject to

¹⁵ *J. Soc. of Dyers and Colorists*, 27, 279 (1911); *Trans. Faraday Soc.*, 16, 116 (1920).

TABLE IV
CAPILLARY CROSS SECTION OF TANGENTIAL SECTIONS

Membrane	V cc. per sec.	Av. P in Volts	100 X	Per Cent Capillary Cross Section of Rays from Photo- micrographs.
Sitka Spruce	0.00453	0.0136	1.97	1.19-1.90
	.00424		1.84	
	.00365		1.59	
Alaska Cedar00148	.0135	0.73	0.79
	.00137		0.67	
Western Red Cedar00080	.0139	0.41	0.39
	.00090		0.46	
Western Hemlock00160	.0132	0.75	0.82
	.00144		0.68	
Douglas Fir00058	.0131	0.30	0.26
	.00044		0.22	
Yellow Poplar00127	.0135	0.58	1.31-2.03

CAPILLARY CROSS SECTION OF TRANSVERSE SECTIONS

	V	Density of Wood	100 X	Max. Capillary from Density
Sitka Spruce	0.0693	0.304	74.3	80.4
	.0552	.408	60.8	73.7
Alaska Cedar0570	.442	61.7	71.5
Western Red Cedar0676	.290	73.3	81.3
Western Hemlock0704	.343	75.0	77.9
Douglas Fir0546	.526	55.0	66.1
Yellow Poplar0176	.320	18.7	79.3

being clogged by resins. Both of these factors tend to cut down the effective capillarity. The results thus seem to show that the electro-endosmotic measurements give a very good statistical value for the effective ray cell capillarity.

The second part of Table IV gives the percentage capillarity cross section of the transverse sections from the electroendosmose measurements, and the maximum capillarity calculated from the density of the wood. The latter is the maximum theoretical capillary cross section on the assumption of all cells being open at both ends, and the capillarity in the other two space directions being negligible. This is equal to $100 \frac{(1-d)}{d_0}$ where d is the density of the wood, and d_0 that of wood substance (1.55 by water displacement). In general the capillarity approaches this maximum value. The observed value for yellow poplar again is low due most likely to the fact that the fibers are shorter than in the case of the softwoods.

The above measurements on the tangential sections seem to indicate that practically all of the effective capillarity can be accounted for by the ray cell capillaries. This makes it seem as though the capillarity

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of a radial section, which contains no ray cell capillarity, would either be small or made up of some other form of capillarity than that of the tangential sections. Though the capillarity of the radial sections is small, it is sufficiently great to warrant the consideration of a small possible ring shake capillarity in addition to that of the increased pit communication capillarity.

The differences in the rates of electroendosmose through the three different kinds of sections seems to be entirely a matter of relative unobstructed microscopic capillarity. The electrical conductivity on the other hand seems to be a surface phenomenon in which the hygroscopic moisture in the submicroscopic structure as well as that on the surface of the capillaries is effective.

Summary.

1. The rate of electroendosmose through membranes of six different species of wood were studied using sections cut in the three different structural directions.

2. Adjacent sections give similar rates. The thickness of the membranes does not affect the rate appreciably for the thin sections used.

3. The potential of wood against water was computed from determinations of the increase in velocity of endosmose resulting from the drilling of a known cross section of holes. A value of approximately 0.0136 volt was obtained for all of the species.

4. The effective capillary cross section of tangential sections, as obtained by the electroendosmotic measurements, corresponds very well with the capillary cross section of the ray cells obtained from photomicrographs.

5. The capillary cross section of the transverse sections approaches a maximum value corresponding to that calculated from the density of the wood on the assumption that all cell cavities are open at both ends, and the capillarity is entirely perpendicular to the transverse plane.

6. The results indicate that the motion of water through the submicroscopic structure is very small. Even the slight capillarity through the radial sections seems to be other than that of submicroscopic structure.

7. The increased specific conductivity of water in wood over that of water in bulk, and the similarity of the ratios of the conductivities in the three different structural directions of wood containing only hygroscopic water with those for wood with all of the capillaries filled with free water indicate that the electrical conductivity is a surface phenomenon.

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THE PLACE OF ADHESION IN THE GLUING OF WOOD

By F. L. BROWNE AND T. R. TRUAX

Although glue gave the name to colloid science and the chief constituents of most of the important glues have been favorite materials for colloid investigations, the ancient art of gluing has until recently been almost completely neglected by scientists. The glues in use at the present time have been discovered chiefly by accident and gluing methods developed by frank empiricism. That a systematic study of the subject will lead to important technological improvements has already been demonstrated in the gluing of wood, and there is reason to believe that better glues are likewise awaiting discovery. If, however, really significant advances are to be made in the development of glues, the colloid chemist must first explain how glues hold wood surfaces together and what are the essential properties of an adhesive.

Bancroft¹ seems to consider that adhesion, in general, depends upon adsorption of the adhesive at the surfaces which are joined, and that the degree of adhesion can probably be measured by the amount of adsorption. In the joining of wood with animal glue, for example, he concludes that the strong force of adhesion between the proteins of the glue and the wood substance brings about a concentration of the proteins at the wood-glue interface, and that among different glues the strongest joints may be expected with the one which is thus adsorbed to the greatest extent and hence offers the greatest adhesion.

McBain and Hopkins,² on the other hand, point out that adhesion is not the only factor determining the strength of a glue joint. The evidence shows clearly that strong joints require the presence of a film of adhesive of appreciable thickness which must transmit whatever stresses may be applied. A glue must therefore be a highly cohesive material in order to provide sufficient mechanical strength. For joining smooth surfaces, such as glass or polished metal, there must of course be a strong force of adhesion between glue and surface, but when porous materials like wood are united it may only be necessary for the glue in the fluid condition to penetrate sufficiently and solidify in place. McBain and Hopkins therefore consider that there are two different types of adhesion—*specific adhesion*, involving a force of attraction between adhesive and surface, and *mechanical adhesion*, involving the

¹ "Applied Colloid Chemistry" (I), 74 (1924).

² Second Report of the (British) Adhesives Research Committee.

embedding of solidified adhesive in the cavities of a porous material. They consider wood joints to be in the latter class.

That mechanical adhesion is operative in the joining of wood with any of the glues now in common use by woodworkers can scarcely be questioned, but the present writers take a middle ground in believing that specific adhesion is also an important factor. This does not imply any serious disagreement with McBain and Hopkins' point of view, but merely a difference in emphasis and perhaps in definition. The penetration of the glue into the lumina and vessels of the wood, which is essential to mechanical adhesion, can be brought about only if the glue while in the fluid condition wets the wood, that is, if the glue sol adheres to the walls of the wood elements. In view of the continuous character of the sol-gel transformation and the drying of the glue jelly, it does not seem probable that this adhesion is entirely lost when the joint dries. Moreover the strongly hygroscopic nature of the common wood-working glues and of the wood substance as well makes it reasonable to suppose that glue and wood possess an attraction for each other. At least some degree of specific adhesion therefore seems to be a *sine qua non* for mechanical adhesion in the case of materials of such a fine degree of porosity as wood.

The difficulty of obtaining mechanical adhesion in wood with a glue which does not wet wood is illustrated by the following experiment: Smoothly surfaced and matched blocks of red oak were selected because the numerous large vessels, free of tyloses, were thought to afford an excellent opportunity for penetration. As the "glue," Lipowitz' alloy was selected because metals do not wet wood and because this alloy, when kept at a temperature slightly above its melting point, 65° C., has a viscosity not unlike that of woodworking glues. The blocks, previously heated, were "glued" together under a pressure great enough to squeeze out excess adhesive and still leave a continuous film of alloy of a thickness comparable to the films found in strong joints with common types of glue. When the joints had cooled thoroughly the blocks were found to adhere with about the tenacity of any smooth, flat surfaces pressed together tightly enough to exclude all air from between them. When the joints were pulled apart by hand the metal film was easily removed intact, and it was found that no appreciable penetration had been obtained even in the largest vessels of the wood.

Two lines of evidence against specific adhesion as an important factor in the gluing of wood are adduced by McBain and Hopkins:

In one set of experiments they applied three coats of an oil stain to the wood surfaces to be joined, presuming that they had thus closed the available openings in the wood. This prevented obtaining satisfactory glue joints in the case of mahogany. With pine, however, the glue joints were reasonably strong. One is free to explain the results

in a different way from that offered by the experimenters. The oil stain may have formed a thin coating over the surfaces of the mahogany, preventing wetting of the wood by the glue. Pine probably absorbs oil more readily, so that the amount of stain applied may not have been sufficient to form an effective barrier between wood and glue. If such experiments are to throw light upon the question of specific adhesion, the "filler" should be impregnated into the wood to a sufficient depth to permit sanding of the surface in order to remove any coating. In this way the cavities will be filled and yet there will be some uncoated wood substance for the glue to wet. We have tried to carry out this scheme with sugar maple test specimens impregnated in one case with paraffin and in the other with collodion. When the specimens were glued together with animal glue and tested the joints made with the paraffin-treated wood failed at an average load of 2,200 pounds per square inch and those treated with collodion at 2,500 pounds per square inch. Microscopic examination of thin sections across the glue joint showed that the amount of penetration of the glue had been very greatly reduced by the presence of the fillers, but that we had not succeeded in preventing penetration entirely. If specific adhesion has no part in the joint strengths obtained, then it would seem that remarkably little penetration of the glue suffices to produce a strong bond.

McBain and Hopkins' second argument against specific adhesion in wood joints rests upon the assumption that adsorption "is an almost necessary inference" in the case of specific adhesion, and they cite some experiments the results of which they interpret as showing the absence of adsorption of gelatin by wood. When dry pine sawdust was brought into contact with a gelatin solution, the solution increased in concentration by an amount which would be accounted for if the wood adsorbed about 24 per cent of its weight of water and did not adsorb any gelatin. Since the amount taken up from pure water was found by direct determination to be about 10 per cent, the conclusion was drawn that any adsorption of gelatin by the wood is negative. However, the authors seem to doubt the reliability of their value for the "adsorption" of water by wood, because they give it with a question mark in their tabulated data. That it is greatly underestimated can scarcely be doubted, since we know that the fiber saturation point for pine lies well above 24 per cent. The data therefore do not justify the conclusion that there was no adsorption of the gelatin.

It should be remembered that wood is a very strongly hygroscopic material absorbing and holding about 30 or 35 per cent of water in an intimate relation probably quite similar to the condition of the water in a concentrated gelatin jelly. When dry wood is placed in an aqueous solution, the absorption of hygroscopic water should be distinguished

from any adsorption effects at the wood-solution interface. Even if one chooses to regard the hygroscopic water as adsorbed in ultra-microscopic cavities, the dimensions of such cavities are presumably of an order comparable with molecular sizes—vastly smaller than the microscopic cavities which we usually have in mind in speaking of wood as a “porous” material. The small, mobile, highly polar water molecules would be expected to penetrate interstices inaccessible to the large, swollen micelles of a gelatin sol. In agreement with this view Salzberg³ finds that an aqueous solution of glucose increases in concentration when brought in contact with sawdust.

But whether adsorption took place in McBain and Hopkins’ experiments or not, the proposition that there can be no adhesion where there is no positive adsorption does not seem acceptable. We may regard adsorption as a matter of the relative attractive force between the material composing the solid surface and the solvent and solute respectively. A stronger attraction between wood and water than between wood and gelatin would express itself in negative adsorption of the gelatin. But such a condition does not indicate the absence of any attractive force between wood and gelatin. On the contrary, since the affinity of wood for water is so great—dry wood will abstract water from calcium chloride monohydrate—its attraction for gelatin may be less and still be large enough to account for a powerful adhesion between the surfaces of wood and the dry glue film of a joint.

The writers are inclined to picture conditions during the making of a glue joint in some such manner as the following: The glue, whether it be animal, casein, blood albumin, starch, or perhaps even sodium silicate, is applied to dry wood in the form of an emulsoid sol of such concentration as is necessary to give a fluid of convenient consistency to spread properly with the woodworker’s machinery and to penetrate the wood cavities to some extent in order to increase the surface area available for adhesion. As already mentioned, penetration will be obtained only if the glue wets the wood. Excessive penetration is undesirable for two reasons,—it wastes glue and may produce “starved” joints. Fortunately the dry wood absorbs water from the glue, such water penetrating to a much greater depth below the surface of the wood than the glue. A microscopic examination of sections through glue joints made with glues of alkaline reaction shows this greater penetration of the aqueous dispersion medium very beautifully, because on staining with phenolphthalein the presence of alkali can be demonstrated far beyond the limits of penetration of the glue jelly. Presumably hygroscopic moisture is drawn in still deeper than the dissolved alkalies.

The concentration of the glue sol resulting from the withdrawal

³ Unpublished data of the Forest Products Laboratory.

of water by the wood, together with the drop in temperature in the case of hot glues, brings about gelation with the desirable results of avoiding excessive penetration of the glue and producing a consistency of the glue in the remaining glue film suitable for withstanding the



FIG. 1.—A section through a joint in oak plywood joined with casein glue showing that the glue moisture carrying sodium hydroxide with it penetrates much farther into the wood than the casein jelly. The alkali stains the wood through reaction with the tannin contained in the wood.

rather high pressures which must ordinarily be employed for bringing about uniform contact of the wood surface with the glue films. It is very important from the point of view of gluing technic to make sure that a suitable balance is maintained between pressure applied to the joint and consistency of the glue film *at the time of pressing*. With a mobile glue film high pressures must be avoided. If a high pressure

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must be used, care should be taken to obtain a firm glue film before applying it.

During the drying of the joint the glue jelly is subjected to severe stresses which the elastic gels are peculiarly fitted to withstand. Both

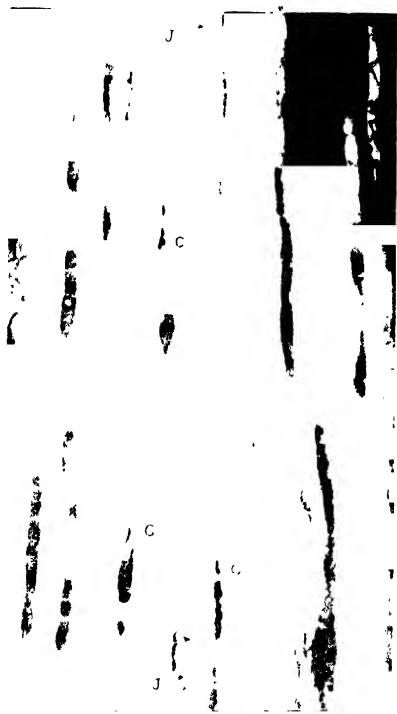


FIG. 2.—A longitudinal section through a "starved" joint, "JJ", showing how the shrinkage of tendrils of glue penetrating the wood cavities takes place by exaggeration of the glue meniscus, making the dry glue tendrils hollow cylinders, "C", for a large portion of their length. Such a large increase in the area of the meniscus could not take place against the force of surface tension if there were no specific adhesion of the glue for the wood.

the wood and the jelly itself shrink, and the volume change must be brought about by a readjustment within the glue film if contact between wood and glue is to be maintained. The shrinkage of wood is 50 to 100 times as great transversely as longitudinally and may be twice as much radially as tangentially. In plywood and panel construc-

tion the grain of alternate plies is placed at right angles, so that the direction of maximum shrinkage in one is opposed to that in the other. The resulting shearing stress upon the glue film during drying should be at least partly compensated by appropriate volume changes in the

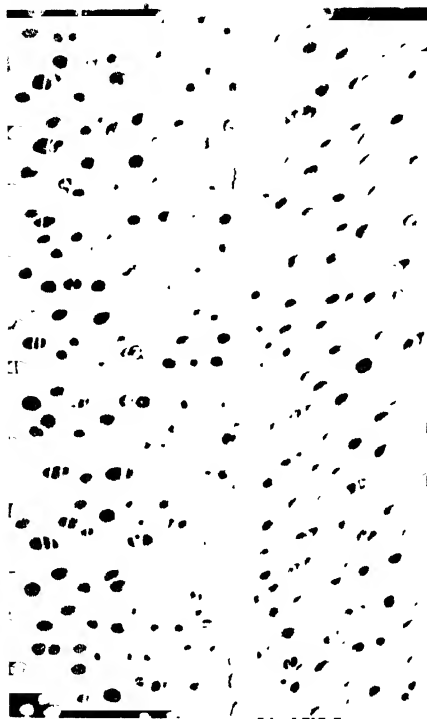


FIG. 3.—A cross section through a "starved" joint showing the relatively deep penetration of glue into the wood and how the glue tendrils form hollow cylinders clinging to the walls of the wood cavities as the glue jelly shrinks. (Observe small white spots, to the left, surrounded by dark rings representing the dry glue.)

jelly, a condition which can be met only by a material which combines high mechanical strength with the ability to flow sufficiently to make volume changes by alteration of its three dimensions in any manner demanded.

It is clear from the foregoing that the peculiar properties demanded of a glue for woodworking are such as are especially characteristic

of those emulsoid colloids which yield elastic jellies. Since there is a manifest need at the present time for a more precise definition of the word "glue," it is suggested that it be based upon a recognition of this fact. McBain and Hopkins make the proposition that "any fluid which wets a particular surface and which is then converted into a tenacious mass by cooling, evaporation, oxidation, etc., must be regarded as an adhesive for that surface." We would accept this, and then define a glue as a particular type of adhesive, as follows: *Any material which can be obtained as an emulsoid sol of suitable consistency, which wets a particular surface, and which subsequently forms a strong elastic jelly by cooling, heating, evaporation, or chemical reaction must be regarded as a glue for that surface.* Such a definition has the advantage of recognizing the newer adhesives which are now known in commerce as glues, and it should commend itself particularly to disciples of Thomas Graham.

That specific adhesion is an important factor in obtaining strong wood joints will be clear on further considering the results of the shrinkage of glue during drying. If the glue did not stick to the wood, the tendrils of jelly projecting into the wood cavities would be expected to shrivel and no longer fill the openings. The glue film between the gross surfaces would also be expected to draw away from the wood, arching over the spaces between the openings into the wood cavities. Microscopic examination proves that such is not the case. Shrinkage of the glue tendrils takes place largely by enormous exaggeration of the concave meniscus at the inner end of the tendril, leaving a film of glue clinging to the walls of the cavity. When dry the tendrils become long, hollow cylinders for a great portion of their length. Shrinkage in the main glue film evidently takes place by a decrease in total thickness, drawing the wood surfaces somewhat closer together than they were at the time the glue "set."

A tradition of the glue room holds that stronger joints result when the smooth wood surfaces are slightly roughened by means of a toothing plane, a claim which has been used as an argument in favor of mechanical adhesion. Careful investigation has shown, however, that under proper gluing conditions smooth joints are at least as strong as "scratched" joints, and that it is only under "starved" joint conditions that the roughened surfaces help to keep pockets of glue which provide a bond over a portion of the contact surfaces and hence give stronger joints. The practical man's prejudice in favor of tooth-planed surfaces has been due to the fact that other traditions of the glue room have favored the production of starved joints.

Microscopic examination of sections of a very large number of glued joints made with many woods, several kinds of glue, and various gluing conditions, the strengths of which had been tested have

led to the conclusions that (1) for strong joints it is necessary to have an observable, continuous film of glue between the surfaces joined, (2) the thickness of the film may vary within rather wide limits without affecting the strength of the joint, and (3) there is no correlation

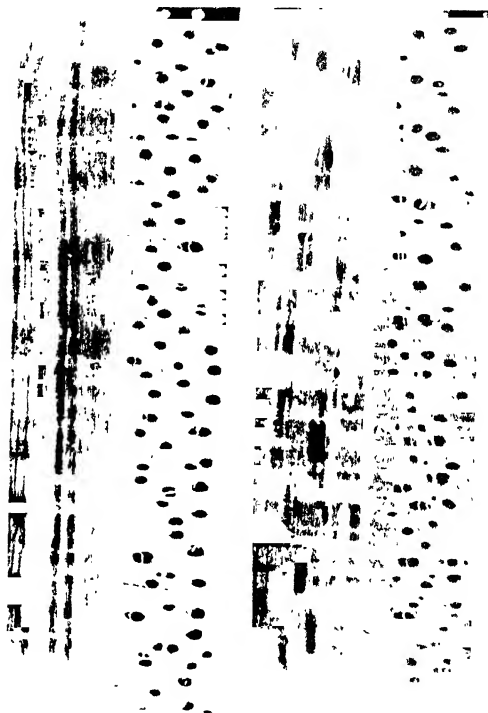


FIG. 4.—Sections through two joints in birch plywood made with the same glue under the same gluing conditions, except that four times as much pressure was applied in one case as in the other. The higher pressure resulted in a thinner glue film and much greater penetration of the glue into the wood cavities, but did not increase the strength of the joint.

between strength of joint and the amount or depth of penetration of glue into the vessels or lumina of the wood.

The necessity for maintaining a continuous glue film between the surfaces is obvious on the basis of either the mechanical or specific adhesion theories, but if mechanical adhesion alone were of importance it should be possible to demonstrate an optimum degree of penetra-

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tion for obtaining the strongest joints. That no such optimum has been found and that with many woods strong joints have been obtained with remarkably little penetration of glue into wood cavities argues strongly that specific adhesion is at least comparable in importance with mechanical adhesion for the gluing of wood.

During the course of a number of experiments involving joint tests, a careful observation was made of the results obtained with blocks in which the grain, instead of running exactly parallel to the

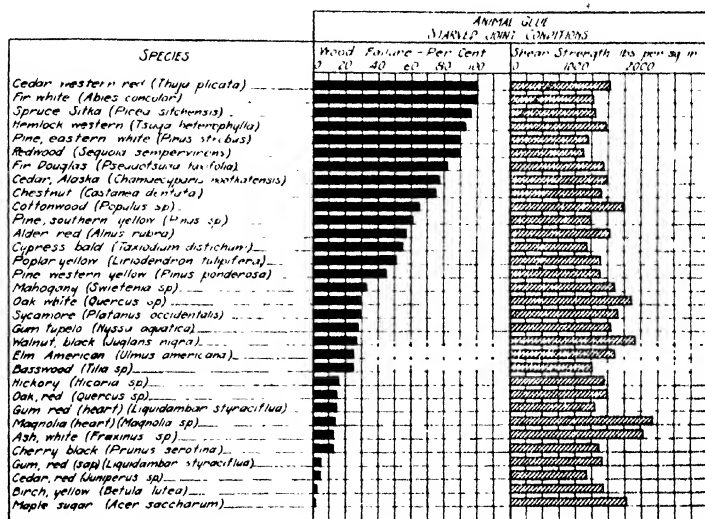


FIG. 5.—The results obtained with animal glue in parallel grain gluing of different woods under "starved" joint conditions.

plane of the joint, made a slight angle with it. If mechanical adhesion alone were effective, one would expect such specimens to give higher test values when the direction of shear is such as to tend to push the glue tendrils, running with the grain of the wood, farther into the wood than when the tendency is to pull them out. No such difference in joint strength in the two cases could be detected.

If mechanical adhesion were the only important factor in gluing wood, there should be a close relation between wood structure and joint strength. The results obtained with a large number of species of wood indicates that, in general, the greater the density of the wood the higher the strength of the joints obtained under suitable gluing con-

ditions. Such a relation might seem to indicate that specific adhesion is more important than mechanical adhesion, but on the other hand it is equally clear that as the density increases the failure tends to take place more largely in the glue film or between film and surface than in the wood. Since our glues are stronger than the wood in shear, the ideal glue joint should fail entirely in the wood and the average proportion of the joint area in which the wood has pulled apart rather than the glue may be taken as a measure of how nearly practice attains to the theoretical ideal. For this reason the density

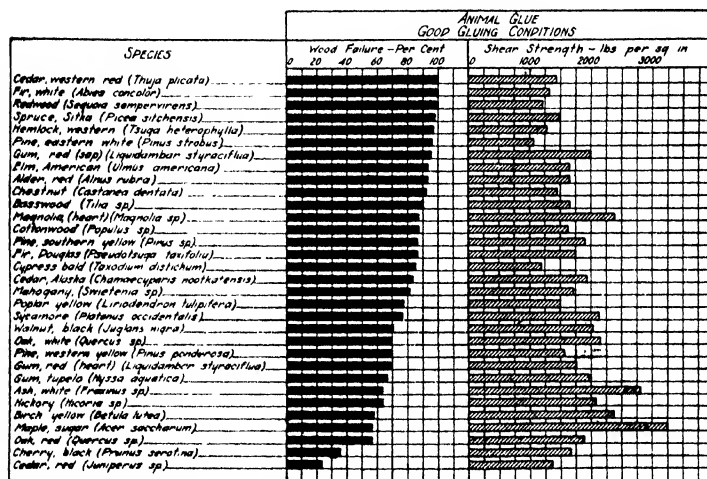


FIG. 6.—The results obtained with animal glue in parallel grain gluing of different woods under good gluing conditions.

relation alone does not throw much light upon the relative importance of specific and mechanical adhesion.

Less ambiguous conclusions can be reached by comparing results obtained with different woods having similar density or structure. If mechanical adhesion alone is operative, the same joint strength and percentage wood failure should be observed in all such cases. On the contrary, very striking differences are found. To begin with, it is found that coniferous woods in general exhibit higher percentages of wood failure than hardwoods of the same density. On the basis of structure and ease of penetration by liquids, the proponent of the mechanical theory would expect the opposite to be the case, because the vessels of the hardwoods offer openings which are usually larger

and more readily permeable than the lumina of the conifer tracheids.

Certain woods have been found to be more difficult to glue satisfactorily than would be indicated by their densities or anything known about their structure. Again, with a number of woods the heartwood is much more difficult to glue than the sapwood. If it be granted that specific adhesion plays an important part in holding wood joints together, these facts find a ready explanation in the influence of the numerous "extractive" materials in woods, but it is very difficult to understand why they should influence purely mechanical adhesion so profoundly. Again, the joint strength of many woods hard to glue can be materially increased by giving the wood a preliminary brush treatment with certain substances such as sodium hydroxide solution. That the alkali removes or alters the chemical nature of extractive materials in the wood which would otherwise interfere with the specific adhesion would account for the results satisfactorily.

Summary.

1. Evidence is offered to show that both mechanical adhesion and specific adhesion are operative in the gluing of wood with the glues commonly used by woodworkers.

2. Specific adhesion between glue and wood does not presuppose positive adsorption of the glue from the sol by wood.

3. The properties required of a material to be useful as a glue for joining wood are such as are peculiarly characteristic of the emulsoid colloids which give elastic jellies, and a definition of "glue" is proposed which recognizes this fact and includes the various materials now used industrially for joining wood.

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METHODS FOR CUTTING AND DIFFERENTIAL STAINING OF MICROSCOPIC SECTIONS OF HARDWOOD GLUE- JOINTS

BY ARTHUR I. WEINSTEIN

In the study of the penetration of glue into the wood on both sides of a glue joint and of the manner of adhesion of different glues under various methods of application, microscopic examination of the glue joints is essential. Satisfactory examination necessitates the cutting of thin, transparent sections of the wood on a microtome and the subsequent staining of the sections. The usual method of preparing wood for sectioning is impracticable for glue joints, in view both of the nonresistance of some of the glues to water and of the possible detrimental effects on the glue of the acids used in the process. Therefore a new technique in the preparation of the material for sectioning and in the staining of the sections had to be developed.

Material and Methods.

The work was done on hard maple joints made with the following glues:

(1) Blood albumin glue; (2) casein glue; (3) vegetable (starch) glue; (4) animal glue (three joints made with animal glue under different gluing conditions). Table I gives the results of strength tests on these joints.

TABLE I

Joint No.	Kind of Glue	Quality of Joint for Hard Maple	Results of Strength Tests	
			Average Strength in Pounds per Square Inch	Wood Failure *
1	Blood albumin	Strong	3080	63
2	Casein	Strong	3521	34
3	Vegetable	Strong	3875	80
4	Animal glue †			
	Joint "a"	Strong	3380	50
	Joint "b"	Weak	2376	10
	Joint "c"	Strong	3617	95

* Estimated on percentage of wood-failure to glue area only.

† "a." Joint made under good gluing conditions. "b." Joint made under "starved" gluing conditions. "c." Joint made under "starved" gluing conditions but wood treated with caustic soda before gluing.

Preparation of Material for Sectioning.

Formalin Method:

The best results with joints of blood albumin, casein, and animal glues were obtained by treating the glue joints with formalin. Parts of the wood containing the joints were cut into small blocks about half an inch long and a quarter of an inch in thickness, and these were placed in glass vials filled with commercial formalin. Some of the blocks sank after twelve hours in the liquid, others floated near the surface for three or four days. After soaking for seven to ten days, longitudinal and cross sections 15 to 20 μ (15 to 20 25000th inch) in thickness were cut on a Thomson modification of the Jung-Thoma sliding microtome.

Alcohol-Glycerin Method:

Very good sections, about 20 μ in thickness, were cut from blood albumin, casein, and animal glue joint "c" (see Table 1) after treating the wood with equal parts of glycerin and 95 per cent alcohol for ten days, followed by formalin for 48 hours. Good sections were obtained by this method from animal glue joint "a," but the glue-line swelled to nearly twice its original thickness. Animal glue joint "b" fell apart before the wood was soft enough to cut.

Hot Alcohol Method:

Equally good sections were also obtained from the blood albumin and casein glue joints and animal glue joint "c" by treating them with hot 95 per cent alcohol for at least 7 days. The method employed was to place the loosely stoppered vials, containing the alcohol and the glue joints, in an electric oven at 70° C. Some of the alcohol evaporated and had to be replaced about every 24 hours.

Hot Glycerin Method:

Sections from vegetable glue joints were obtained by treating the joint with hot glycerin for about five days. The stoppered vials with the glycerin and blocks were kept in the electric oven at 70° C. for the necessary length of time, after which sections 15 to 20 μ in thickness were cut with ease. The vegetable glue joints could not be sectioned successfully when treated with formalin, alcohol-glycerin, or hot alcohol because they fell apart after only a few hours in the reagents.

Blood albumin and casein joints also yielded excellent sections when treated with hot glycerin, but the animal glue joints all disintegrated, joint "b" falling apart in less than two hours.

Staining.

Since some of the glues are transparent and cannot be clearly identified under the microscope in unstained sections, the use of stains to bring out the glue line becomes a necessity. Stains ordinarily employed in wood technology are of little use, as they stain the glue line the same color as the surrounding cell walls and the various cell inclusions, such as gums, mucilage, etc. In order to identify the glue line unmistakably as it penetrates the wood, the glue must be stained a color distinctive from that of the wood elements. Such a differential stain for hardwood (angiosperm wood) glue joints is Pianze IIIb,¹ which stains the wood green and the glue deep rose to purplish blue. Blood albumin glue is not stained at all, but the brown glue line itself is in this case in fine contrast with the bright green wood.

In staining with Pianze IIIb the sections are placed in the stain directly from the alcohol in which they are cut. After fifteen minutes in the stain they are washed in 95 per cent alcohol, destained with acid alcohol if necessary, and washed again in 95 per cent alcohol to remove the acid. The sections are then run through absolute alcohol

TABLE II

Glue Joints		Preparation for Sectioning and Kind of Sections Obtained				Staining with Pianze IIIb 15 to 30 minutes	
No.	Kind of Glue	1 Part Glycerin 1 Part Alcohol (95%) Applied Cold				Color of Wood	Color of Glue
		Hot Glycerin 5 Days at 70° C.	Hot Alcohol 95% 7 days at 70° C.	10 Days, Then 48 Hrs.	Com'l Formalin (Cold)		
1	Blood albumin	Good	Good	Good	Good	Green	Brown
2	Casein	Good	Good	Good	Good	Green	Rose to purplish Rose
3	Vegetable	Good	None	None	None	Green	Rose
4	Animal glue Joint "a"	None	None	Good (somewhat swollen)	Good	Green	Rose
	Joint "b"	None	None	None	Fair	Green	Rose
	Joint "c"	None	Good	Good	Good	Green	Purplish to blue

¹ Pianze is prepared as follows: Malachite green, 0.5 g.; acid fuchsin, 0.1 g.; "Martius elb," 0.01 g.; water, distilled, 150 cc.; alcohol (95 per cent), 50 cc.

² "a." Joint made under good gluing conditions. "b." Joint made under starved gluing conditions. "c." Joint made under starved gluing conditions but wood was treated with caustic soda before gluing.

and xylol and mounted in balsam. The wood is colored a bright green; the glue, brown for blood albumin, deep rose for casein, vegetable, and animal glue joints "a" and "b," and purplish to blue for joint "c."

A summary of results in the preparation of the material and staining of sections is given in Table II.

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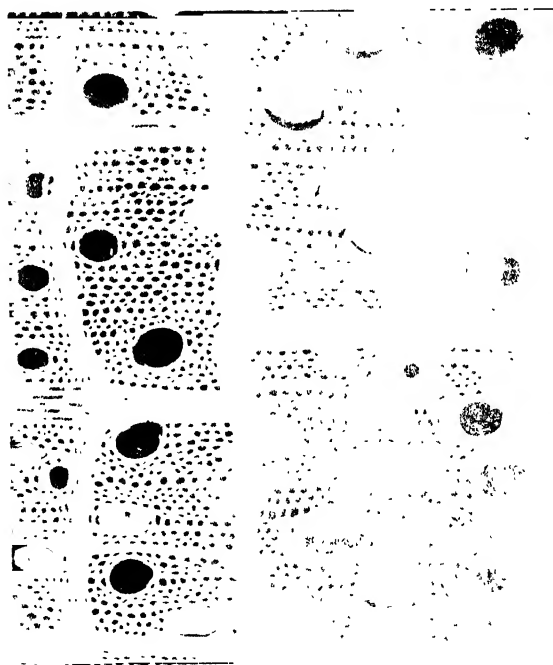


FIG. 1.—Stained cross section of hard maple-blood albumin glue joint. $\times 100$.

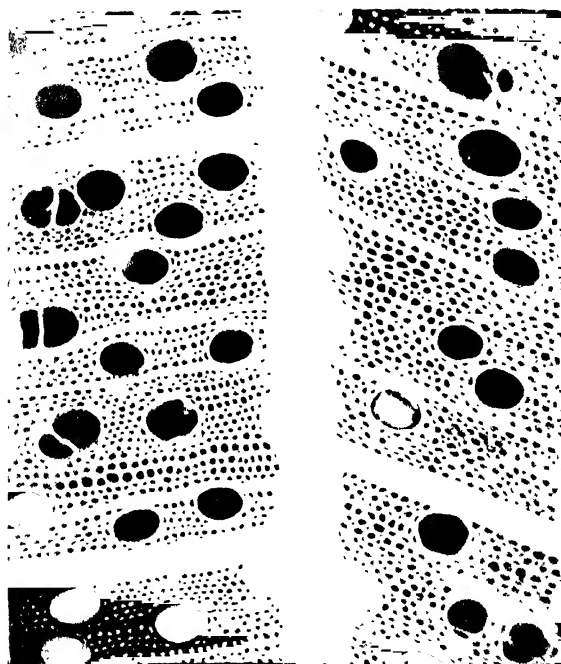


FIG. 2.—Stained cross section of hard maple-casein glue joint. $\times 100$.



FIG. 3.—Stained cross section of hard maple-vegetable glue joint. $\times 100$.



Fig. 4.—Stained longitudinal section of hard maple-animal glue joint "a," made under good gluing conditions. $\times 100$.

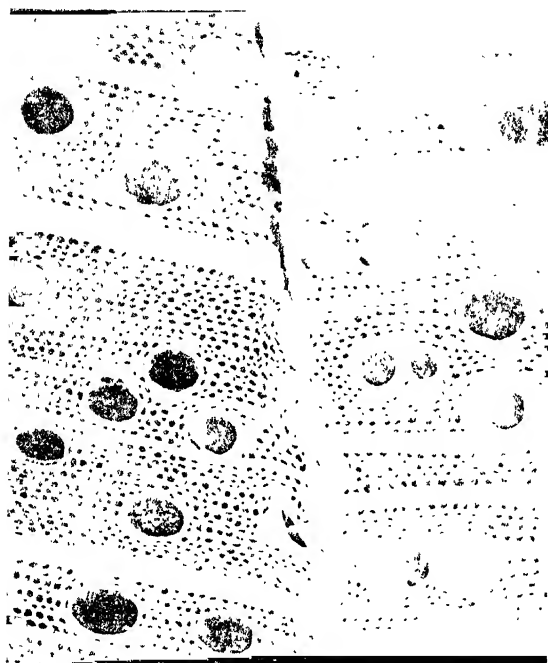


FIG. 5.—Stained cross section of hard maple-animel glue joint "h," made under "starved" gluing conditions. $\times 100$.

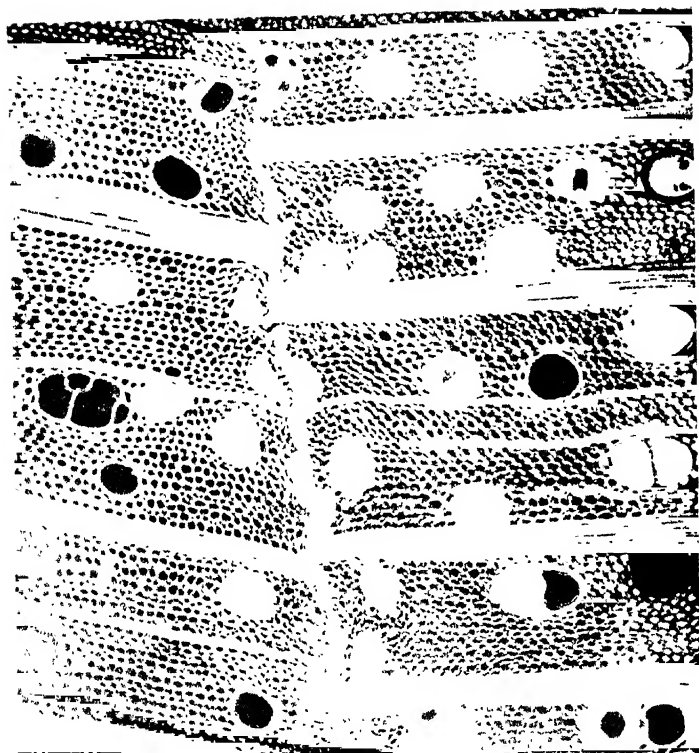


FIG. 6.—Stained cross section of hard maple-animal glue joint "c," made under "starved" gluing conditions but wood treated with caustic soda before gluing. $\times 100$.



FIG. 7.—Stained longitudinal section of hard maple-animel glue joint "c," made under "starved" gluing conditions but wood treated with caustic soda before gluing. $\times 100$.

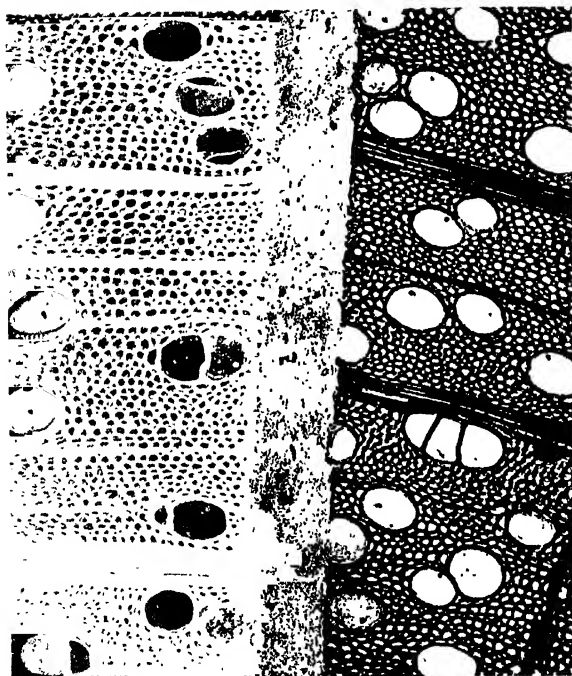


FIG. 8.—Unstained cross section of hard maple-animal glue joint "a," showing faint outline of glue line. $\times 100$.

FLOCCULATION AND DEFLOCCULATION OF THE SILVER HALIDES¹

By S. E. SHEPPARD AND R. H. LAMBERT

At the first meeting of the Colloid Symposium in 1923, one of us presented a paper on "The Dispersity of the Silver Halides in Relation to Their Photographic Properties."² It was stated at that time that grain size and distribution are important factors of the photographic sensitivity of silver halide emulsions and in one and the same emulsion the sensitivity increases as the size of grain increases. Grain size is not, however, a sufficient condition for sensitivity but is apparently a necessary one.

In a paper³ given at the Colloid Symposium last year, it was shown that one very important factor for the sensitivity of photographic emulsions is the inherent sensitivity substance present in the gelatin surrounding the grains. Minute traces of organic isothiocyanates and thiocarbamides in gelatin react with the silver halides to form nuclei of silver sulfide which in turn act as sensitivity centers for light decomposition of the silver halide grains. Theoretically it is therefore possible to separate the process of ripening into two distinct phases, viz., the production of silver halide grains size and composition, and having a given size distribution, and the sensitization of these by inoculation with silver sulfide.

In the paper on "The Dispersity of the Silver Halide, etc.," and in a subsequent paper in *The Photographic Journal*⁴ a tentative theory was sketched by one of us of the process of precipitation which might lead to the size distributions observed in this Laboratory. The fundamental assumption made was that the distribution of ionic and molecular velocities in the reacting solutions is representable by Maxwell's "error function." Accordingly, the number of ions having velocities between the limits v and $v + dv$ will be

$$dn = CN e^{-\frac{3}{2} \frac{v^2}{\bar{v}^2}} v^2 dv$$

Where N = total number of ions per unit volume

\bar{v}^2 = mean-square velocity

C = constant (at constant temperature)

¹ Communication No. 279 from the Research Laboratory of the Eastman Kodak Company.

² Colloid Symposium Monograph, 1, 846 (1923).

³ Colloid Symposium Monograph, 3, 76 (1925).

⁴ Sheppard, *Phot. J.* (1925).

It was further supposed that the velocities (of Brownian movement) of the first formed colloidal particles of precipitate formed would be similarly distributed, and that as a first approximation, stirring only affected the constant C .

Since the observed frequency curves are better represented by an equation of the error function type with a logarithmic exponent,⁶

$$y = Ae^{-k \ln(x-a)^2}$$

an extension of the initial premise was necessary. It was pointed out that the type of distribution observed would be obtained if each primary particle surviving at the time t_0 grew at a rate proportional to its size.

These suggestions were criticized by F. F. Renwick⁶ as inadequate, and particularly as neglecting the electrostatic coagulation or precipitation of silver halide hydrosols originally stabilized by momentary and local excess of a common ion. Renwick indeed goes so far as to state. "Furthermore, Lottermoser showed that AgBr, when precipitated in presence of excess of alkali halide, is negatively charged, while it is positively charged in presence of excess of AgNO₃. When therefore the reacting solutions are approximately chemically equivalent, we should expect instant precipitation and the production of approximately equal numbers of positively and negatively charged primary particles. Such a state of affairs, however, can readily be imagined to be unstable, and we may reasonably expect these oppositely charged *primary* particles *quickly to aggregate to large grains* by electrostatically attracting one another."

"In this manner, it is easy to picture the process of AgBr emulsion grain formation as essentially an electrical precipitation or coagulation process regulated mainly by the concentrations, both absolute and relative, of the two reacting solutions at each instant, and in each minute volume of the mixture."

In reply to this article of Renwick's it was again pointed out that the process of electrical precipitation would only lead, *per se*, to the formation of secondary particles, a reversible process, and not to large crystalline grains, formed by recrystallization. It is the array of crystalline grains which the size distribution curves portray. So far as definitely microcrystalline precipitates of the silver halides are concerned, the phase of "electrostatic precipitation" can only be a subordinate aspect, and one to some extent already considered as the stage of "encounters between (primary) grain and grains, as well as between particles and ions."⁷ None the less, the process of "electrostatic precipitation or coagulation" is of definite importance in regard to the

⁶ Cf. Wightman, Trivelli, and Sheppard, *J. phys. Chem.*, **28**, 529 (1924).

⁷ *Phot. J.*, **48**, 324 (1924).

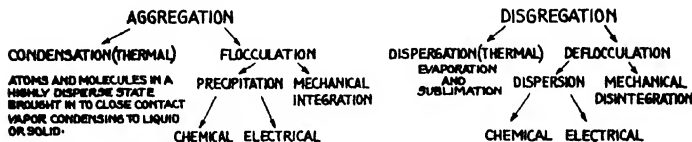
⁸ Cf. also Wightman, Trivelli, and Sheppard, *Trans. Faraday Soc.*, **19**, 73 (1923).

grain formation and growth of silver halides. It is with this phase of silver halide dispersions that this paper is primarily concerned.

Sol formation may and should be regarded as a phase in the crystallization and recrystallization process. This phase may be deliberately extended and separately studied. From this viewpoint a knowledge of the mechanism of the somatic growth of crystals is of the greatest importance and it has been known for a long time that presence of foreign material in the neighborhood of growing crystals may entirely alter their form and size.

The terminology of colloid chemistry, not least in what concerns the formation and dissolution of precipitates, is still very confused. We have thought it well therefore to present a scheme in which our own terms are defined, and particularly those referred to in the title under the antithesis "Flocculation and Deflocculation."

Table I



We understand by condensation and dispergation, changes of state in which a relatively large heat interchange takes place and since in a study of silver halides we are not directly concerned with such changes of state little more will be said about them. Of none of the aspects of aggregation and disaggregation of matter is it true that it is independent of the others. It seems desirable therefore to include chemical, electrical and mechanical aggregation into one term which may be called *flocculation* and that the opposed action be designated as *deflocculation*.

Experimental.

With the various aspects of deflocculation and flocculation in mind, we may proceed to study this process more in detail.

Renwick's contention that the "electrostatic coagulation" is the whole story of grain formation in photographic emulsions appears to be easily rebutted. This process, *in the absence of gelatin* or other protective colloid, leads only to the reversible formation of secondary and tertiary particles or clumps, which are readily redispersed either mechanically or chemically (electrostatically).^{*} Such clumps or clots may, as is well known, be produced as follows:

^{*} The mutual flocculation of oppositely charged hydrosols, postulated by Renwick, follows the same process as the flocculation of a colloid by an electrolyte. Electric neutralization is followed by coagulation of the "neutral" particles by each other.

Potassium bromide is slowly added to silver nitrate in a definite manner while stirring until the equivalent point has almost been reached but silver nitrate is still present in excess. The precipitate falls to the bottom of the beaker. Then the precipitate is washed repeatedly with distilled water until no cloudiness of the wash water could be observed. A sample of the precipitate is then placed in a gelatin coating solution and coated onto a subcoated plate. Figure 1, No. 1, shows a photograph of the grains in a clumped condition. On close inspection, the surface appears very grainy and therefore a photograph in reflected light was taken, Figure 1, No. 2. It can be seen that the nearly round clumps appear, at least in the surface, to be made up of very small individual crystals.

If some of the coagulated material be placed in the palm of the hand and carefully triturated with the thumb of the other hand, a mechanical disintegration such as observed in Figure 1, No. 3, has occurred. In fact experience has shown with sufficient mechanical treatment all the large clumps can be disintegrated.

Instead of mechanical disintegration, one may introduce potassium bromide into the wash water above the coagulated silver bromide grains to a proper concentration. After stirring the material for some time and finally allowing irresolvable aggregates and large crystals to settle, it will be found that much of the coagulum has redispersed. Figure 1, No. 4, shows such a dispersion due primarily to chemical and electrical action. The mechanical action of stirring has very small effect in this case. Since the chemical and electrical effects are hard to separate they are considered together as precipitation and dispersion effects in the preceding diagram.

A study of washing conditions was next attempted since it is known that either silver nitrate or potassium bromide will peptize silver bromide and that the soluble salts adsorbed to the grains exert their peptizing action on washing. To follow this a measurement of turbidity was made after each washing, the latter being performed in a definite manner.

Two hundred cc. of 1 N potassium bromide solution were added at a definite and constant rate to three hundred cc. of silver nitrate solution of such a concentration that 0.25 per cent of the silver nitrate was still left after adding all the potassium bromide solution. The temperature was kept constant throughout the mixing. The silver bromide was almost completely precipitated. The supernatant liquid was then made up to one liter with distilled water and stirred for exactly ten minutes. After settling five minutes a sample of the suspension was measured for turbidity. The supernatant liquid was then decanted and a liter of distilled water was placed over the precipitated silver halide. The stirring and settling procedure was repeated in



FIG. 1.

the same time intervals and the turbidity of the wash water again measured. This was repeated until further washing showed no turbidity.

The turbidimeter used was one in which a light filament placed below a column of suspension could be viewed from above.

By varying the height of the column a point would be found at which the filament would just disappear. The reciprocal of this height

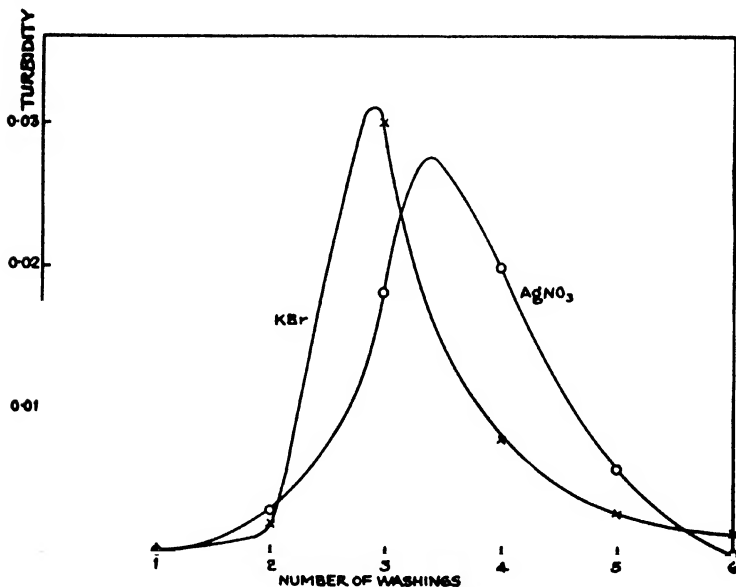


FIG. 2.

in mm. was taken as a measure of turbidity. Since the suspensions were composed of primary particles only and all of approximately the same size, turbidity is a direct measure of the amount of silver halide in suspension.

A second experiment in which the procedure of mixing was exactly reversed was now carried out. Silver nitrate was now added to potassium bromide ultimately leaving an excess of the latter equal to the silver nitrate excess in the first experiment. Washing followed by turbidity measurements was carried out as before and the two experiments thus obtained are graphically recorded in Figure 2. Turbidity is shown as the ordinate while the abscissa represents the number of washings of one liter taken. It will be seen that the turbidities reach

about the same maximum value but not necessarily at equal number of washings.

Since it is known that both potassium halide and silver nitrate peptize the corresponding silver halide, it was decided to test the reversibility of the phenomenon. The mixing experiments were performed exactly as before after which electrical conductivities of the wash waters were taken corresponding to definite turbidities. When

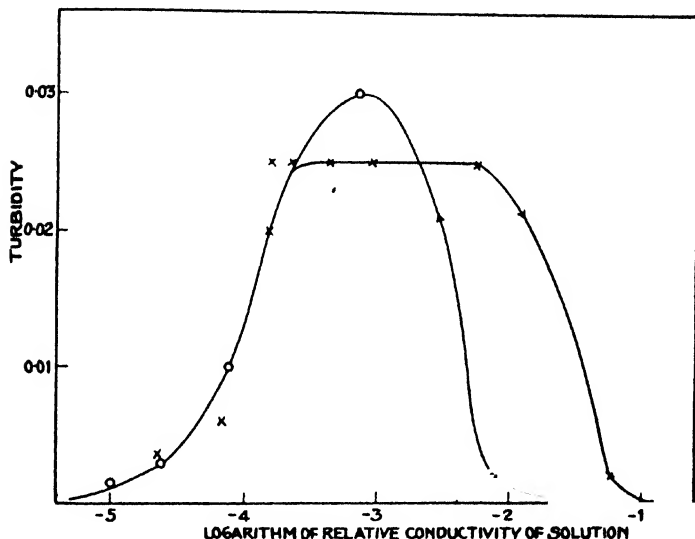


FIG. 3.

the final wash water showed no turbidity it was not decanted but successive amounts of silver nitrate in the first experiment and of potassium bromide in the second case were added, the system stirred and the coagulum allowed to settle, as before, after each addition.

The peptizing effect of silver nitrate is entirely irreversible as shown by absence of turbidity on its addition to the thoroughly washed silver bromide. Later it was found that potassium nitrate present after mixing in the manner described above, has no peptizing and probably no coagulating effect on the silver halide. It does not influence the action of silver nitrate on the silver bromide.

Potassium bromide disperses silver bromide reversibly, as shown in Figure 3, in the case of freshly precipitated material. It was found, however, that although potassium nitrate has no noticeable effect on

this reversible action, it absolutely prevents peptization if added to thoroughly washed silver bromide before potassium bromide is added.

An interesting experiment was now performed in which potassium bromide was added to silver nitrate. In one case potassium bromide was left in excess and in a second case silver nitrate was

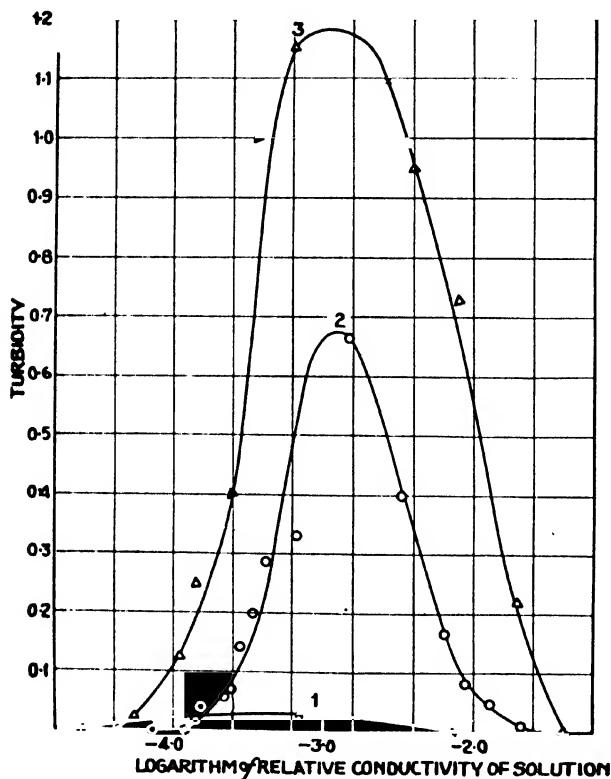


FIG. 4.—Curve 1, KBr always in excess; Curve 2, KBr left in excess; Curve 3, AgNO_3 kept in excess.

kept in excess. Washing was carried out as before. Successive amounts of potassium bromide were now added and conductivity and turbidity measurements were secured. These experiments together with peptizing experiments by potassium bromide in which potassium bromide was always in excess during mixing, were plotted on the same graph for comparison. Figure 4.

Undoubtedly the manner of treating the coalesced material before washing is of extreme importance. Attempts to peptize by silver nitrate in like manner gave only negative results.

The effect of gelatin on the appearance of turbidity was but briefly studied at this time. Silver halide was prepared as previously by keeping silver nitrate in excess throughout during mixing. After washing and peptizing to a maximum with potassium bromide, gelatin

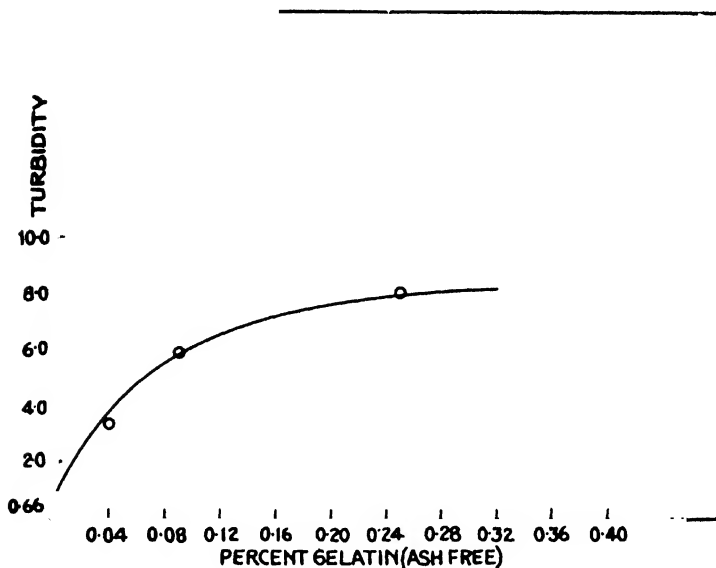


FIG. 5.

was added and turbidity observations were made. Figure 5 gives increased turbidity with increase of gelatin content. The amount of silver bromide in suspension at the highest turbidity observed corresponds to approximately 0.3 normality. Experiments were now carried on using exactly the same method of mixing and washing throughout, *i.e.*, potassium bromide was added to silver nitrate ultimately leaving silver nitrate slightly in excess in each case, but adding other common or closely related ions after washing in order to study their relative peptizing power. Figure 6 shows the resulting data. It is interesting to note that potassium chloride disperses equally as well as potassium bromide but potassium iodide does not. Ammonium bromide and

hydrobromic acid are equal as dispersing agents but fall far short of the chloride and bromide of potassium.

Nitric acid, ammonium hydroxide and potassium hydroxide failed to disperse at all and all have a detrimental effect on dispersion by potassium bromide when in their presence. The effect of valency of the cation of the electrolyte is still to be studied.

In studying the deflocculating effect of the common ion electrolyte, attention was necessarily drawn to the researches of Lottermoser⁹ on coagulation phenomena with silver iodide as the disperse phase

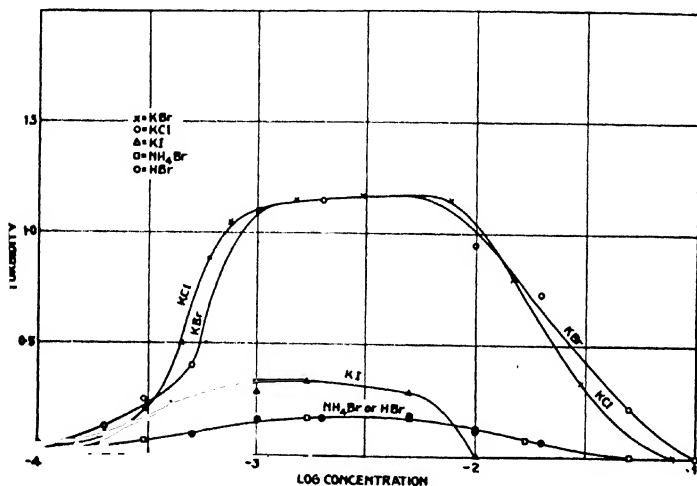


FIG. 6.

and of Jablczynski¹⁰ on the rate of coagulation of the silver halides. Although the two authors do not agree as to the mechanism of coagulation, the experiments of both are valuable. Lottermoser's data refer principally to the point of complete flocculation as a function of composition when mixing solutions of silver nitrate and alkaline halide. This point he calls the "Klarpunkt."

Figure 7 gives comparisons of the clearing points of silver halides as obtained by us in the case of bromides and chlorides and by Lottermoser for the iodides. Perhaps an elucidation of Lottermoser's "clearing point" is in order to explain the nature of these experiments. If

⁹ *J. prakt. Chem.*, **72**, 39-56 (1905); *Z. Physik Chem.*, **62**, 284-286, 358-383 (1908); *Kolloid-Z. (Zsigmondyfestschrift)*, **36**, 230-237 (1925); *Z. angew. Chem.*, **39**, 347-356 (1926).

¹⁰ *Bull. soc. chim.*, **33**, 1892-1425 (1923). *Ibid.*, **35**, 1277-1292 (1924).

the electrical potential of a silver salt solution be measured with a silver electrode¹¹ as the amount of potassium halide is added a curve such as shown in Figure 8 will be obtained. The clearing point, as

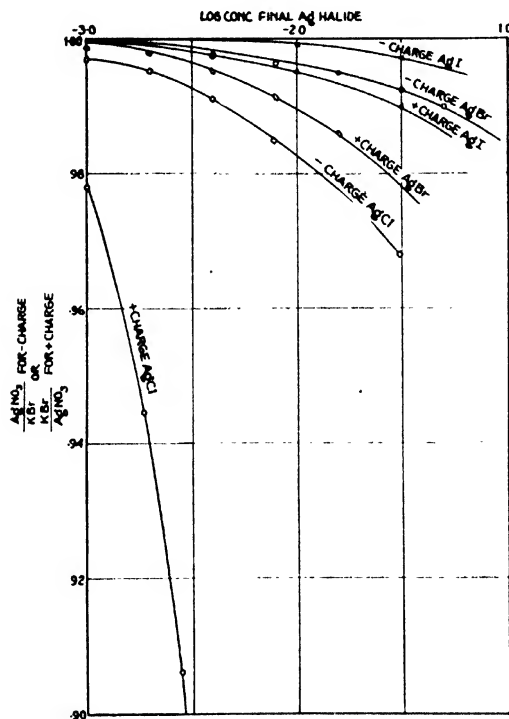


FIG. 7.

indicated by the arrow, appears during titration, by rapid stirring, before the point of equivalence. The location of this point depends on the concentration of the reacting solutions and approaches the equivalent point with decreasing dilution. It lies closer to the equivalent point for excess halide than for excess silver nitrate when equal concentrations of reacting solutes are employed. The Volhard method

¹¹ Cf. Müller, "Die Elektrometrische Mass Analyse," p. 85 et seq. (Steinkopf, Dresden, 1928). It is important to notice in this connection that in the titration of potassium iodide with silver nitrate the potentials in the neighborhood of the inflexion point show an increasing inconstancy, only vanishing when the titration endpoint is exceeded. This inconstancy is reduced by powerful agitation. It is less with bromide than with iodide, and practically absent with chloride. This inconstancy of potential is due to removal of reacting ions by adsorption and flocculation.

does not necessarily correspond to the electrometric titration¹² the deviation being greater the lower the concentration of bromide. The "clearing point" corresponds, as change of state of aggregation, to the color changes of indicators in the titration of acids and bases. In the latter case, the color change for a given indicator may occur well away from the electrochemical equivalence point. The relation of Lottermoser's "clearing point" to the "critical potentials"¹³ of the systems Ag Hal: water (solution) and Ag Hal: glass, is not known with certainty. It was observed that when titrating potassium bromide solution with silver nitrate, the capillary effect, *i.e.*, adhesion of AgBr to the glass wall, occurred practically at the "clearing point" at all

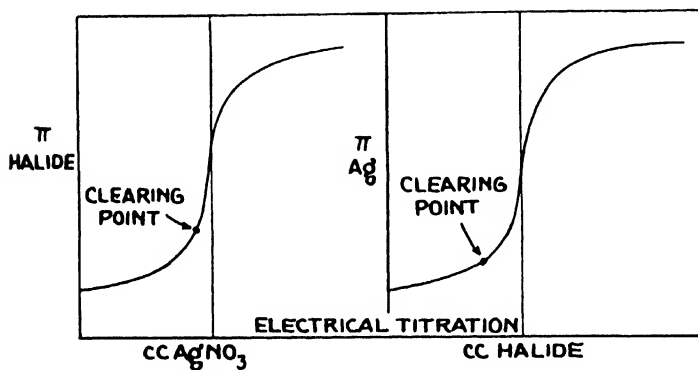


FIG. 8.

concentrations. But on titrations in the reverse order, the capillary effect preceded the clearing point, the more the concentration. In any case the "clearing point" corresponds only to an arbitrarily determined stage in the process of coagulation, generally of rapid coagulation. One may distinguish a threshold of coalescence of colloidal particles ultra-microscopically, again a visibility threshold of coalescence as initial turbidity, finally a "clearing point" of complete coagulation. Even so the process is *not* terminated absolutely, as is shown by the phenomena of "adsorption reversal" and aging of precipitates.¹⁴

Lottermoser's explanation of the coagulation, of the silver halides, which is substantially Renwick's theory of the grain formation in gelatino-silver-halide emulsions, is one of purely electro-adsorption, or as termed by Fajans¹⁵ contact-adsorption. An excess of adsorbed

¹² Cf. Muller, *loc. cit.*

¹³ Cf. Freundlich, "Kapillarchemie," 325 et seq., 342 (1922).

¹⁴ Freundlich, "Kapillarchemie," 622 (1922).

¹⁵ Fajans and Beckerath, *Z. physik. Chem.*, 97, 478 (1921).

positive or negative ion charges the particles and makes them stable. When there is excess of neither the anions Cl^- , Br^- or I^- , the neutral particles coagulate to large secondary particles and the colloid precipitates.

Jablezyński¹⁶ objects to this on the ground that it does not sufficiently explain the velocity of increase of turbidity in the presence

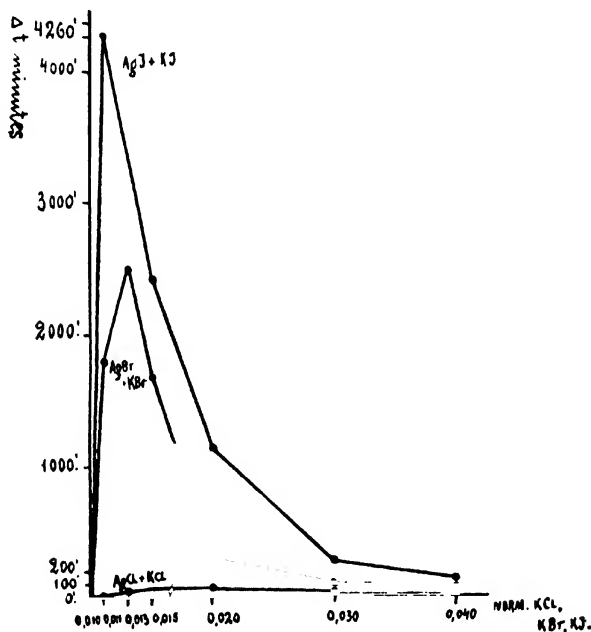


Fig. 9.

of gelatin or other protective colloids. These inhibit flocculation even at low concentrations. Jablezyński's method of experiment was to rapidly mix in a test tube 5 cc. of a solution of AgNO_3 with an equal volume of KCl , KBr , or KI , and determine the time for a visibility mark on the back of the tube to disappear. That is, he measured the time for production of a fixed turbidity. The value Δt he took as being the reciprocal of the mean velocity of opacification. In presence of excess of KCl , KBr , KI respectively, results for the three corresponding silver salts were obtained shown in the graph reproduced.

¹⁶ *Bull. soc. chim.*, 33 (2), 1392 (1923).

This type of curve he explains as follows: At first excess of the alkaline halide reduces the ionization of the silver salts and their solubility, hence at first the velocity diminishes; in the second period, further excess of the soluble halides increases the solubility of the silver salts by formation of double unstable salts of the type $KAgBr_2$, etc. The diffusion from grain to grain (Ostwald ripening) accomplishes itself therefore not only by the ions and non-ionized molecules of the silver salts, but also by those of the double salts. Hence the diffusion velocity increases, and the period Δt diminishes.

Jableczyński obtains the same type of curve in the presence of gelatin. This result, together with the effects of ammonia and of increase of temperature in reducing the period Δt he advances as refuting the coagulation theory. As against this, he regards the silver halides as forming colloids of the *second order*, distinguished from the sols of the metals, the sulfides, and the oxides, by being more or less soluble in water. The formation of precipitates, and the process of grain growth for the silver halides is envisaged by Jableczyński as entirely a process of recrystallization by solution of the smaller grains and growth of larger ones at their expense (Ostwald ripening¹⁷) until the larger grains are thrown down. The decisive factor in this case is the *diffusion* of material from the smaller to the larger grains.

Consider the equation for vapor tension of liquid droplets of radius r

$$p = p_0 + 2 \frac{ag}{Gr} \quad I$$

Where p_0 = vapor tension at plane surface

g = density of vapor

G = density of liquid

a = surface tension of liquid.

From this

$$p = p_0 \left(1 + 2 \frac{aM}{RTG} \cdot \frac{1}{r} \right) \quad II$$

Where M = molecular weight of vapor

R = gas constant

T = absolute temperature.

Considering the process of solution as analogous to evaporation, we can replace in equation II the vapor pressure by concentration C .

$$C = C_0 \left(1 + \frac{A}{r} \right) \quad III$$

Where C = concentration of solution about a grain of radius r

¹⁷ Cf. Trivelli and Sheppard, "The Silver Bromide Grain of Photographic Emulsions," Monograph No. 1 on Theory of Photography, etc., 58 et seq.

C_0 = concentration for plane surface of massive substance
above plane surface

A = constant.

The difference of concentration about two grains of radii r_1 and r_2 is then

$$C_1 - C_2 = AC_0 \frac{r_2 - r_1}{r_1 r_2}. \quad \text{IV}$$

The mean velocity of increase of turbidity (supposed due to increase in grain size) is expressed by the amount of substance transferred by diffusion in the time Δt .

$$V = \frac{\Delta X}{\Delta t} = \frac{kD}{Z^n} (C_1 - C_2).$$

Where D = coefficient of diffusion

Z = mean distance between grains

n = constant.

This equation expresses some of the facts semi-quantitatively, but cannot be regarded as entirely adequate.¹⁸ Thus the analogy between the solution of small crystals and the evaporation of liquid drops is not so close that the same equation can be applied, with certainty. The small solid particles are not spheres, but crystals, with different faces behaving in a different manner.¹⁹ It is doubtful therefore whether the radius difference has the specific significance attributed. However, Jablczynski's main contention that grain growth with the silver halides is chiefly due to recrystallization deserves full consideration. Our own observations appear to show that in the precipitation of the silver halides, in the absence of gelatin and similar protective colloids, two processes are taking place, one involving the adsorption and coagulation postulated by Lottermoser, the other the recrystallization process. The contention of Jablczynski that the process is entirely a matter of recrystallization is contradicted by the evidence of reversible flocculation and deflocculation of part of the silver halide precipitates in washing (cf. Figures 1 to 4).

The microscopic appearance of the precipitates is also evidence that a process of coagulation has produced secondary and higher order aggregates of loosely adhering primary particles, evidently by the process of electrolytic coagulation. (Figure 10.)

It is precisely the existence of crystal aggregates in the precipitates from the silver halides, which are not readily "repeptized" to individual crystals either chemically or mechanically, which indicates that both

¹⁸ Only at high temperatures does crystallization velocity approach a diffusion velocity Cf. Marc, *Z. physik. Chem.*, 77, 614 (1911)

¹⁹ Cf. Trivelli and Sheppard, "The Silver Bromide Grain of Photographic Emulsions," Monograph No. 1 on Theory of Photography, etc.

processes are operative. Under high power microscopic examination, the precipitates of the silver halides show, as soon as the reacting concentrations are above a certain value, individual crystals as in

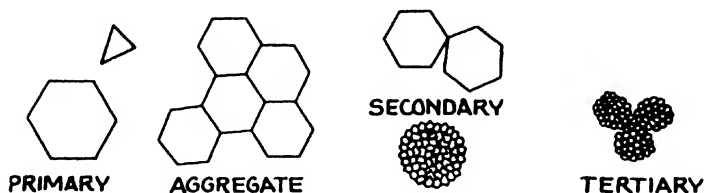


FIG. 10.—Primary particles, crystals, aggregates and particles of higher order. (Diagrammatic.)

Figure 11. But in addition there appear aggregates illustrated in Figure 12. These aggregates are not the "secondary particles" of various authors,²⁰ which are composed of primary particles (crystals)

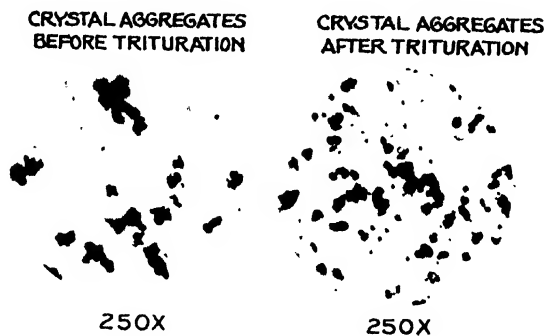


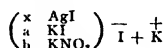
FIG. 12

FIG. 11.

held together by the electrostatic and hydration forces of the electrical double layers surrounding them, *i.e.*, their electrical double layers are in common equilibrium.²¹ Such secondary, etc., particles are readily disgregated or deflocculated, unless they undergo "aging." In the case

²⁰ Cf. Mecklenburg, *Z. anorg. Chem.*, **64**, 368 (1909).

²¹ The (hydrated) electrical double layer plays essentially the same part as a protective colloid of the protein or carbohydrate type. Its formation and constitution cannot be discussed here, but are partly recognized, *e.g.*, Lottermoser's formulation of the colloid silver iodide particle as



of the silver halide the "secondary particles" pass readily into crystalline aggregates, and aggregate crystals, which again are not completely stable on prolonged digestion in the presence of excess alkaline halide.

In the presence of gelatin or similar colloids,²² the coagulation is largely inhibited, at least until very much higher concentrations of the reactants are employed. The observation of Kenwick²³ does not disagree with this, because in preparing silver bromide emulsion the concentrations are necessarily high. The inhibiting effect of such colloids on the flocculation of silver iodide has been used by Lottermoser to determine a "silver iodide number," analogous to Zsigmondy's "gold number." Hence it may be concluded that the process of coagulation instanced by Kenwick plays only a small part in the formation of the silver bromide grains of photographic emulsions, at least of negative emulsions. The grain growth is primarily due to a process of recrystallization from solution,²⁴ in which crystal aggregation plays a small part. When Jablzyński²⁵ states that "Les colloïdes de second ordre *coagulent* même en présence du colloïde stabilisant, comme ils ne perdent pas leurs charges, ils portent leur substance des grains plus petits aux plus grands par la solution, la voie de diffusion," he appears to us to be correct in the main fact, but inexact in the use of the term coagulation.

Analogy Between Recrystallization and Coagulation.

In an important paper²⁶ Jablzyński followed experimentally the increase in optical density²⁷ with time of precipitating silver halide (AgCl, AgBr). He found the relation between the density and the time to be linear of the form

$$D = D_0 + Kt$$

By an application of Rayleigh's equation for light transmission in turbid media²⁸ he shows this reduces to

$$\frac{1}{n} - \frac{1}{n_0} = Kt$$

or

$$n = \frac{n_0}{1 + Kn_0t}$$

where n is the number of grains at a time t , n_0 the original number per unit volume. He points out that this equation is of the same

²² Cf. Lottermoser, *loc. cit.*

²³ *Loc. cit.*

²⁴ Cf. Sheppard, 1st Colloid Symposium Monograph, *loc. cit.*

²⁵ *Bull. soc. chim.*, 35, 1286 (1921).

²⁶ *Ibid.*

²⁷ Measured in a König Marten spectrophotometer for green light

²⁸ *Phil. Mag.*, 41, 107 (1874)

form as that deduced by Smoluchowski²⁹ for the rapid coagulation of colloids of the first order. He considers, however, that the mechanism is *completely* different in the two cases.

We have already discussed the relation of the two processes. It appears, however, that *kinetically* considered the two processes have very considerable similarity.

In the case of electrolytic coagulation, as considered by Smoluchowski, the theory is based on the probability of collision of (equal sized) two particles, all collisions being supposed inelastic. In the case of recrystallization, the principal process is probably the collision of two particles viz., a diffusing *ion* and a crystal particle or nucleus, later of a diffusion ion with a crystal presumably larger than a nucleus. It might be expected therefore that the recrystallization process would follow, at any rate initially, a course representable by Smoluchowski's formula, in its general form

$$\frac{1}{n} - \frac{1}{n_0} = kt.$$

In some experiments on the recrystallization process by digestion in excess of aqueous potassium bromide of rapidly precipitated silver bromide, results were obtained in agreement with this. Equivalent silver nitrate and potassium bromide solutions were rapidly mixed in a special apparatus.³⁰ The reaction being accomplished in about 40 seconds for 200 cc. of each solution. 100 cc. of a solution of potassium bromide was added, and the system digested at 60° C. (which was also the temperature of precipitation) with constant stirring of about 1200 r.p.m. Decreasing speed to 200 r.p.m. was not found to affect the results appreciably. The precipitation was carried out in .625 per cent of ash free gelatin solution, which on dilution with the aqueous potassium bromide made the concentration during digestion .50 per cent. The silver bromide was 0.5 N at mixing (9.4 per cent) and 0.4 N during digestion (7.5 per cent).

Samples were withdrawn at given time intervals, and photomicrographs made from one grain layer.³¹ From these, counts of the numbers of grains per unit volume were made.

TABLE II
DIGESTION CONDITIONS

No.	Concentration of KBr	Ratio of KBr : AgBr
1.....	.02 N	2:40
2.....	.04 N	4:40
3.....	.06 N	6:40

²⁹ *Z. physik. Chem.*, **92**, 129 (1917).

³⁰ This followed in principle Jolibois' apparatus for rapid mixing [*Compt. rend.*, **169** (1), 95-8 (1919)]. Cf. also *Proc. Roy. Soc.*, **104** A, 374 (19—), and will be described elsewhere.

³¹ Made by A. P. H. Trivelli.

The results are shown in the graph (Figure 13).

It will be seen that there is a linear relation between the reciprocal of the number of grains and the time for a considerable period of the digestion process, after which the experimental values fall away from the theoretical linear relation.

It is noteworthy that the deviation becomes marked not when the number of grains has decreased to any fraction of the original but when a certain time has passed.

The reason for the falling off of the rate at which grains disappear is probably due to approaching exhaustion of the grains small enough

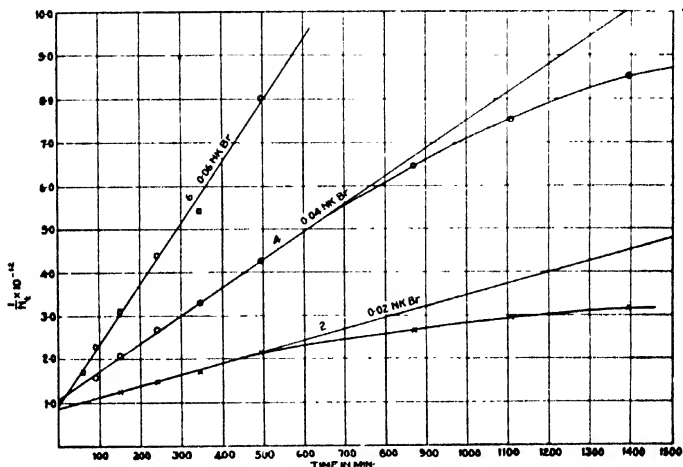


FIG. 13.

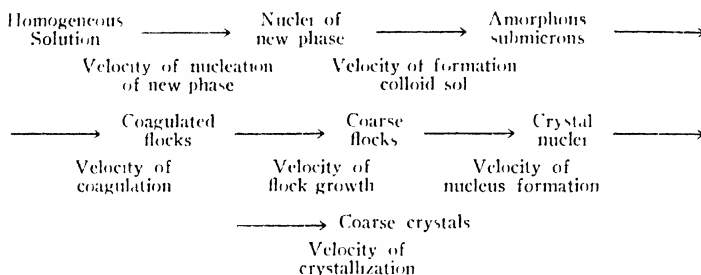
to have a solubility excess. At the same time, the surfaces of the growing crystals are changing, and in particular the fast growing cubic surfaces are being eliminated and the slowly growing octahedral surfaces left. In this digestion process it may be assumed that coagulation, in the sense of Lottermoser's work, is practically completely absent.

We may mention that the relation of coagulation and recrystallization processes is critically discussed by H. Freundlich²² in his monumental "Kapillarchemie." He says "it is still a question in what relation the velocity of growth of coagulated flocks stands to velocity of crystallization in the ordinary sense. It may be that germs of the crystalline phase must first appear in the flocks, which then grow with

²² "Kapillarchemie," 680 (1922).

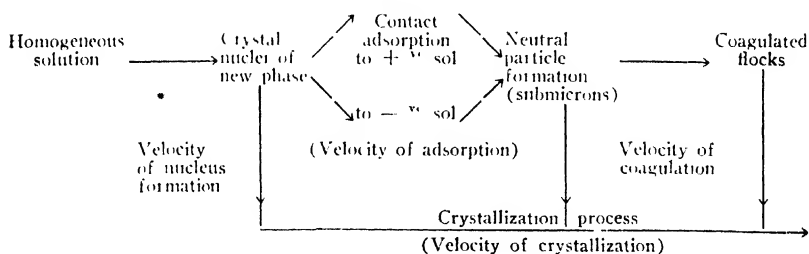
their proper crystallization velocity. One would then possibly have in the genesis of a crystalline solid precipitate in a solution the following chain of processes:

TABLE III



Freundlich adds "It remains uncertain, whether one has the right to differentiate between the growth of the flocks (flocculation) and the actual crystallization, and whether the same constants have not to be considered in both cases." In the case of the silver halides, it appears to us that the nexus of crystallization and flocculation is somewhat different from that suggested by Freundlich. X-ray spectrographic examination of the colloid sols and gels of the silver halides shows these to be micro-crystalline from their first appearance. The primary particles of any flocks in this case are therefore crystalline, and the relation of coagulation and crystallization is therefore more probably somewhat as follows:

TABLE IV



The relation of crystallization and coagulation according to this are in a somewhat different order in regard to time. Reversible flocculation depends upon the formation and coalescence of hydrated adsorption layers at the surface of crystals, corresponding to a temporary inhibition of crystal growth. The decoalescence or rupture of the

hydrated adsorption layers leads to crystal aggregate formation, otherwise the flocculation is completely reversible, and as shown by Oden and Ohlson¹⁴ the number of particles on deflocculation is the same as before flocculation. We have in the sedimentation process¹⁴ a method of testing the extent to which reversible flocculation and irreversible coagulation, leading over to crystal growth, are present respectively. We are making a further study by this method of the precipitation of the silver halides.

Summary.

1. The relation of coagulation and recrystallization in the grain growth of silver halide precipitates is discussed.

2. Evidence is given that coagulation by electro-adsorption is a phase of silver halide precipitation, in agreement with Lottermoser. The process is not purely one of recrystallization, as suggested by Jablezyński.

3. The coagulation due to electro-adsorption is inhibited by gelatin. The higher the concentration of gelatin the higher the total concentration of reactants at which flocculation is possible.

4. Electrocoagulation and recrystallization follow at first the same law for the diminution of number of particles.

5. Electrocoagulation and flocculation play only a subordinate rôle in the grain growth of silver bromide emulsions.

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Rochester, N. Y.

¹⁴ *Z. physik. Chem.*, **82**, 78 (1913)

¹⁴ Oden, *Kolloid Z.*, **26**, 100 (1920)

PECTIN JELLIES

By Miss G. SPENCER

The usual statement in regard to pectin jellies is that we have to have a more or less definite relation between sugar, acid and water for a given pectin content in order to get a jelly. With low acid and high acid a syrup is said to be formed and also with high and low sugar.

The first step toward a theory for jelly formation seemed to be to get a qualitative view of the jelly field. Starting with 1 gram of Douglas Pectin per 100 grams of jelly, the sugar-acid ratio was varied. The results as obtained in Professor Bancroft's Laboratory are shown qualitatively in the following diagram:

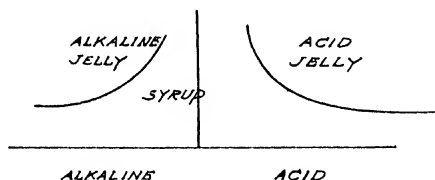


FIG. 1 - Constant pectin; ordinates are sugar content

From this it appears that there are two jelly fields, one in the acid region and one in the alkaline.

Investigation has been centered on the acid jellies, the edible jellies, and most workers have found that when the sugar was increased beyond a certain point a syrup or weak jelly resulted. In our experiments we carried the sugar concentration even up to the point at which crystallization made further addition of sugar impossible. At no point was there the slightest tendency toward syrup formation, so crystallization and not syrup formation fixes the upper boundary of the acid jelly field.

Jelly failure resulting from high sugar concentration, as reported, is the result we believe of hydrolysis. In accord with this it was found that the jelly forming properties of a pectin mixture containing the so-called "optimum" amount of sugar can be weakened and finally destroyed by boiling. The fact that some workers report weak jellies where others report syrups is explained by the higher degree of hydrolysis in the syrups than in the weak jellies.

Mixtures high in acid are also said to give syrups or weak jellies. In our experiments the acid was increased to several times the acidity for which jelly failure had been reported. At no degree of acidity was there any tendency toward a weakening of jellies as the acidity was increased. Again it can be shown that the formation of syrups in mixtures high in acid, as reported, is a result of hydrolysis. Mixtures which give firm jellies, even optimum acidity mixtures if sufficiently boiled lose their jelly forming property. At very high acidities, decomposition of pectin will take place without heat. This instability of pectin and not a limiting acidity for gelation will fix the right hand boundary of the acid jelly field.

These experiments show that the acid jelly field is a continuous one above the syrup jelly boundary, and that syrups exist only below the boundary. The syrups or weak jellies reported for high acid and sugar concentrations are due to the experimental error in hydrolysis.

We do not know the quantitative value of this boundary line between the syrup and jelly field because pure pectin has not been prepared and there is no doubt that the salts held by impure pectin influence the curve.

Work on other colloids and some of the work on pectin implies that pectin jelly formation might be an isoelectric precipitation. It is obvious that both the acid and alkaline fields cannot represent isoelectric jellies. We have carried out cataphoresis experiments to see if the jellies in the acid field are isoelectric. The results of these experiments show that in every case the pectin is positively charged. In fact the pectin which we used showed a positive charge at the acidity outside of the acid jelly field. Since the isoelectric point is not within the acid jelly field the jellies cannot be isoelectric jellies.

A theory for acid jelly formation then, need not concern itself either with the isoelectric precipitation of pectin or with syrups at high acid or sugar above the boundary line. The theory must explain the boundary line separating the syrup field from the jelly field.

As a working hypothesis for a theory of pectin gelation, we are assuming that pectin is peptized by water, that acid displaces water to some extent and that sugar replaces both water and acid to some extent. By the partial displacement of water by acid, followed by the further displacement of water by sugar, the boundary of the jelly region is accounted for because we have decreased sufficiently the amount of absorbed water which is the real peptizing agent.

Thus when acid is low, more sugar is required to form a jelly than when acid is high.

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CATAPHORESIS, ELECTRICAL CHARGE, CRITICAL POTENTIAL, AND STABILITY OF COLLOIDS

BY H. R. KRUYT, A. C. W. ROODVOETS, AND P. C. VAN DER WILLIGEN

Colloid chemistry of today is based entirely on the connection between the electrical charge and the stability of the colloidal particles. This relation was first discovered by Hardy,¹ was confirmed by Burton,² and was later made more definite by Powis.³ Measurements of the electrical surface-charge in connection with the stability of the colloidal particles are of the greatest importance and, when combined with data on the cataphoresis of colloidal solutions, must give the most needed information as to the nature of colloidal solutions. Recently one of us⁴ has shown what difficulties there are in exact measurements of cataphoresis and this paper gives chiefly the results of a study of cataphoresis in which as far as possible all objections to the technique are avoided. We have chosen the arsenious sulfide sol as the one to study, because Powis⁵ obtained results with this very sol which seemed to conflict with his theory of the critical potential, while, on the other hand, the theory described the behavior of other sols extremely well. Powis found that the critical potential, based on cataphoresis experiments in presence of potassium chloride did not agree with that which he had found with other electrolytes, such as barium chloride, aluminum chloride, thorium nitrate, etc. We first attempted to get a better agreement by avoiding, so far as possible, all the errors in the cataphoresis technique. From our results it will be seen that we have succeeded in getting a better agreement between theory and fact, but the outcome is quite different from what we had anticipated.

Experimental Part.

We have made our experiments in Burton's apparatus. The most difficult question to answer is what liquid shall be in contact with the sol.⁶ The liquid must have the same conductance as the sol, so that the fall of potential shall be uniform throughout the whole tube. Also it must contain the same electrolyte as occurs in the intermicellar liquid.

¹ *Z. physik. Chem.*, **33**, 385 (1900).

² *Phil. Mag.* (6), **11**, 423; **12**, 472 (1906); **17**, 582 (1909).

³ *Z. physik. Chem.*, **89**, 91, 186 (1915).

⁴ *Kruijt, Kolloid Z.*, **37**, 358 (1925).

⁵ *J. Chem. Soc.*, **109**, 734 (1916).

⁶ *Cf. Mukherjee, Proc. Roy. Soc.*, **103A**, 102 (1923).

It seemed therefore best to use as the other liquid the ultra-filtrate from the sol itself. In this way it was possible to avoid a diffusion potential at the surface between the sol and the other liquid, since this surface was the one to be watched in the experiment. We have made use of membranes of collodion which had been dissolved in alcohol-ether and not of collodion which had been dissolved in glacial acetic acid, so as to avoid contamination by electrolyte. The membranes were precipitated in the new, porous porcelain, filters of Bechhold-König,⁷ which have functioned admirably in our experiments.

We have first proved that we actually get the intermicellar liquid in this way and that adsorption by the membrane causes no appreciable change. When doing ultra-filtration, the first 200-300 cc. that came through were always thrown away. When we speak later of the ultra-filtrate, we shall always mean the liquid that comes through after the first 200-300 cc.

A solution of two millimols KCl per liter was filtered through a membrane made from 1.5 per cent collodion. The solution itself had a specific conductance of $K_{25} = 2.31 \times 10^{-4}$, and the ultra-filtrate one of 2.32×10^{-4} . An arsenious sulphide sol, to which sufficient potassium chloride was added to give a concentration of 20 millimols per liter, had a specific conductance of $K_{25} = 29.5 \times 10^{-4}$ while the ultra-filtrate showed 29.2×10^{-4} . The sol itself had a specific conductance of about 2×10^{-4} ohms⁻¹ and was a little better conductor than the ultra filtrate.

$K_{25}/\text{sol } 2.10 \times 10^{-4}$	ultra-filtrate 2.05×10^{-4}
$K_{25}/\text{sol } 2.10 \times 10^{-4}$	ultra-filtrate 1.93×10^{-4}
$K_{25}/\text{sol } 2.10 \times 10^{-4}$	ultra-filtrate 1.79×10^{-4}

In addition it was established that different ultra-filters—made with 1, 2, 3 or 4 per cent collodion—gave identical ultra-filtrates for the sol (with and without an added electrolyte).

We may therefore draw the following conclusions:—

1. By ultra-filtration we actually get the intermicellar liquid.
2. The specific conductances of the sol and the ultra-filtrate may differ by several per cent in consequence of the conductance of the particles in the sol.
3. If an electrolyte is added to the sol, the difference between the conductance of the sol and that of its ultra-filtrate is small.

By this method of measuring the cataphoresis we always satisfy the conditions that the clear liquid is identical with the intermicellar liquid and that the resistance is uniform throughout the apparatus. This is most nearly true at the higher concentrations of the electrolyte

⁷ Bechhold and Gutlobn, *Z. angew. Chem.*, 37, 494 (1924).

but the error is small even with the pure sol or with the lower electrolyte concentrations.

Measurements.

The solutes used were prepared in the usual manner.⁸ The determinations were always carried out in duplicate and triplicate with the cells in parallel. The voltage was read on a voltmeter; as the source of current we used the city direct-current circuit at 220 volts with a lamp in series. The distance between the electrodes was always 23 cm.

With the pure sol the intermicellar liquid was placed above the sol; in the other determinations the intermicellar liquid was brought to the same electrolyte concentration as the sol. One might think that one should first add the electrolyte to the sol and then do ultra-filtration; but actually it makes no difference which one does first. If the sol plus 20 millimols potassium chloride per liter is filtered, we find:

$u = 4.10 \mu \frac{\text{volt}}{\text{cm.}}$. If the sol is filtered and potassium chloride is then

added to make a concentration of 20 millimols per liter, we find:

$u = 4.10 \mu \frac{\text{volt}}{\text{cm.}}$.

In each run the current was allowed to flow in one direction for ten minutes. The circuit was broken and the two levels measured, after which the current was allowed to flow for twenty minutes in the opposite direction, and then readings were made as before. The dividing surfaces remained sharp even when high concentrations of the electrolyte were used. This was undoubtedly due to the absence of diffusion.

In the following tables the rate of cataphoresis u is given in microns (μ) per second and per volt potential drop. In Table IV are the flocculation values for the sols used.

TABLE I
KCl added

Concentration in Millimols per Liter	u Sol I	u Sol II
0.....	2.45	2.43
5.....	3.44	3.60
10.....	—	4.06
20.....	4.10	4.16
40.....	—	4.23
55.....	4.33	—
66.....	4.47	—

⁸ See Krutz and van den Spek, *Kolloid-Z.* 25, 1 (1919). Also the determinations of the flocculation values were carried out as described.

TABLE II

BaCl₂ added

Concentration in Millimols per Liter	ζ^u Sol II
0.....	2.43
1.....	1.63

TABLE III

K₄Fe(CN)₆ added

Concentration in Millimols per Liter	ζ^u Sol III
0.....	3.13
20.....	4.76
60.....	5.07
100.....	5.09

TABLE IV

FLOCCULATION VALUES

Electrolyte	Sol I	Sol II	Sol III
KCl	80	77	--
K ₄ Fe(CN) ₆	--	--	130
BaCl ₂	--	13	--

Discussion of the Results.

The cataphoresis measurements are shown graphically in Figure 1. From this we see that the curve for barium chloride falls sharply but that the curves for potassium chloride and for potassium ferrocyanide first rise with increasing concentration and show no sign of falling off. We have carried the measurements as far as possible so as to get as near to the limiting value as possible, because we expected originally that the curves would eventually fall off. This seems not to be the case and the results seem at first sight to lead to a conclusion very much in conflict with the point of view which we outlined at the beginning of this paper.

We are always inclined to assume that the potential of the double layer is proportional to the rate of cataphoresis, in accordance with the Helmholtz formula as modified by Debye.

$$\zeta = \frac{6\pi\eta}{HD}u$$

where ζ is the potential, η the viscosity, H the drop of potential, D the dielectric constant, and u the rate of cataphoresis. Generally we assume that the small concentration of electrolyte can have no appreciable effect on η or on D .

For two reasons we believe that this assumption is not strictly true. We have here to deal with the friction and the dielectric constant in the

electric double layer at the surface of the particles, where the concentration becomes a good deal higher owing to the adsorption. Even though the viscosity and the dielectric constant do not change appreciably in the dilute solution, it is not certain that the high concentration in the adsorption film may not have quite an effect. We are also not certain that the dielectric constant remains unchanged in dilute solutions. Walden⁹ has recently published some experiments which show that the addition of a salt to a pure liquid usually causes a lowering

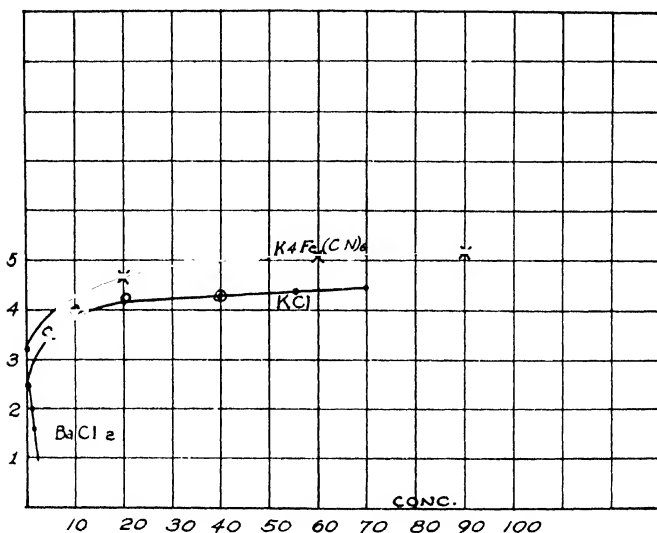


FIG. 1.

of the dielectric constant, passing through a minimum with increasing concentration and then increasing to a value higher than that for the pure solvent. Walden found this the regular thing with different organic solvents. With water he could only get the first fall. Fürth¹⁰ has carried the curve further and finds that the minimum is reached with five millimols potassium chloride after which an increase occurs.

In the formula as given we certainly cannot consider D as constant but we must assume that the curve for μ lies for the most part above that for ζ (Figure 2). With barium chloride ζ falls so rapidly that the dielectric constant is scarcely changed at all. The dotted line for ζ

⁹ Walden, Ulrich and Werner, *Z. physik. Chem.*, **116**, 261 (1925).

¹⁰ *Physik. Z.*, **25**, 676 (1924).

coincides fairly closely with the solid line for u and the agreement will undoubtedly be much closer for aluminum chloride and thorium nitrate.

The surprising result of our experiments and reasoning is first that the rate of cataphoresis, when determined under the best conditions, does not decrease when a univalent cation is added, u increasing at first. Other investigators have found the same thing when multivalent anions are present. Powis¹¹ obtained a fall in the u line for potassium chloride and considered the course of the u line to be the same as that of the ζ line, so that he found no agreement with his own theory of the critical potential. The recent investigations, which have shown the change of the dielectric constant with the concentration, prove that the potential falls much more rapidly than had been assumed, and proves that we cannot yet calculate ζ in the case of higher concentra-

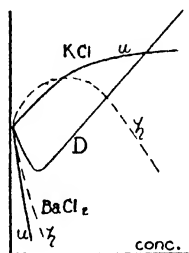


FIG. 2.

tion of electrolytes. We also see from these considerations how cautious we must be about deciding against the theory of critical potentials on the basis of experiments like those described. On the other hand the correction due to the change in D is in just the right direction to account for the lack of agreement which has existed between the calculated potentials when colloidal solutions are precipitated by multivalent and by univalent cations.

Various other investigators¹² have found these same difficulties and have criticized the theory of the critical potential¹⁴ because of this. Nevertheless, nobody has put forward a viewpoint which explains the colloid-chemical phenomena so well as the theory of Hardy and Powis. It is unfortunate that we cannot make a final statement so long as we do not yet know the change of the dielectric constant in concentrated salt solutions; but that can be determined. From the present measurements we cannot say definitely where the maximum is in the potential curve

¹¹ *J. Chem. Soc.*, 109, 734 (1916).

¹² Powis, *loc. cit.*; Freundlich and Zeh, *Z. physik. Chem.*, 114, 65 (1925); Limburg, *Dissertation*, Delft (1924).

¹⁴ Limburg thinks that the electrical conductance plays as important a part as the charge

for univalent electrolytes. Two of us¹⁴ have recently proved that the so-called antagonism of the ions depends on the fact that one of the electrolytes shows a maximum. When one considers how satisfactory is the agreement which Powis has obtained for the critical potentials in the case of multivalent ions, one must admit that the maximum concentration in the case of the antagonistic action is a sure sign of the occurrence of a maximum in the potential curve.

Conclusions.

Cataphoresis measurements with Burton's apparatus have been made with an arsenious sulfide sol, using the intermicellar solution as the other liquid. The rate of cataphoresis increases with the addition of potassium chloride in all concentrations up nearly to the flocculation point. On the basis of recent investigations on the dielectric constant it is recognized that there actually is a fall of potential on adding an electrolyte, and that the rate of cataphoresis u does not necessarily vary in the same sense as the fall of potential ζ . Since the critical potential does not depend on a definite u value but on the value of u/D , there is no justification for rejecting the theory of critical potentials.

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¹⁴ Kruyt and van der Willigen, *Verh. Konink. Akad. Wet. Amsterdam*, **34**, 1240 (1926).

THE DE-INKING OF PAPER

BY T. R. BRIGGS AND F. H. RHODES

Introduction.

The de-inking¹ of printed paper is a problem in detergent action and as such it is of interest to colloid chemists. Being an important step in the commercial recovery of used paper, it has given rise to a large number of patents—some more than forty years old—but so far as the present authors are aware, no quantitative laboratory investigation of de-inking has yet been published. The problem has accordingly been taken up in the Cornell Laboratory and the present paper is a report on the results which have been obtained up to the present time. The problem has been considered so far entirely from the point of view of detergent action and little effort has been made to guide the investigation along the lines of technical practice.

In de-inking paper the ink is dislodged from the cellulose or other fibers and is brought into suspension in a liquid medium, with which or from which it may be removed. The first stage of the process is one of dispersion, and, since the printed paper is a more or less solid complex of pigment, oil, size, and fiber, a suitable mechanical treatment (pulping) in the presence of a peptizing agent (detergent) will be necessary. In general, the peptizing agent may be an ion or a colloid in solution; the most effective detergent is a substance or a combination of substances which is able not only to peptize the carbon-black (or other pigment) of the ink, but also to emulsify, dissolve, or otherwise attack the oily vehicle of the ink and to aid in the disintegration of the paper. When brought into suspension, the carbon-black may be removed with the liquid dispersion medium by washing the latter out of the pulp, or it may be allowed to pass into a second liquid, such as an oil, which wets carbon preferentially, or it may be adsorbed at a liquid-liquid or liquid-vapor interface and be removed by flotation. All of these methods have been tried in practice.

A large number of detergents have been recommended for de-inking. Alkaline reagents form an important group, especially sodium hydroxide, sodium carbonate, sodium silicate, and borax. The hy-

¹ Baskerville and Joyce, *J. Ind. Eng. Chem.*, **13**, 214 (1921); Baskerville and Stevenson, *ibid.*, **18**, 213 (1921); Joyce, *Met. Chem. Eng.*, **25**, 242 (1921); Haas, *Chem. Ztg.*, **45**, 1187 (1921); Wells, *Paper*, **30**, 7 (1922); Payne, *Met. Chem. Eng.*, **29**, 1176 (1923); Berl and Pfannmüller, *Z. angew. Chem.*, **39**, 887 (1925).

droxyl ions presumably peptize the ink by adsorption and they may also attack the vehicle of the ink if the latter contains saponifiable oils, forming soaps which are themselves active de-inking agents. Colloidal detergents which have been recommended include the soaps, together with other materials, such as those contained in spent sulfite liquor, extract of sea-weed, or in the products of enzyme action. Finely divided solids have also been employed in de-inking, particularly silica, alumina, fullers' earth, bentonite, whiting, and calcium silicate. Oils such as turpentine, kerosene, or pine-oil, have been used in discharging the adsorbed ink from the fibers and in collecting the ink in the pulp. Scum flotation and froth flotation have been recommended as a means of separating the ink from the pulp in an effort to render washing the pulp unnecessary.

The present investigation had as its immediate object a comparative study of a number of typical detergent substances, in order that some information might be gained as to their effectiveness in de-inking paper. It was necessary therefore to develop a technique by which de-inking could be carried out conveniently in the laboratory and determined quantitatively. The procedure that was finally adopted is described below.

Procedure.

Ordinary newsprint, made available through the cooperation of the *Ithaca Journal-News*, was employed throughout this investigation. For the purpose of obtaining uniformly representative samples of printed paper in the various experiments, a large supply of a single issue of the above publication was torn into small pieces and the whole was thoroughly mixed. A quantity of the unprinted stock used in the above issue was prepared in the same way.

In general the procedure was simple. A weighed portion of printed paper was disintegrated (pulped) in a solution containing the de-inking agent. The paper was then recovered in the form of a cake of wet pulp and the latter was washed free of detergent and peptized ink. Sheets of paper were next prepared, dried, and pressed flat. The whiteness² of these sheets was finally determined by means of a Taylor "reflectometer."³ From the whiteness, in turn, the amount of de-inking accomplished by the detergent could be ascertained quantitatively and thus expressed as a definite number.

Pulping was carried out in a square glass jar (12 cm. on each side, 24 cm. high) or in a rectangular lead vessel (11 cm. on each

² "Whiteness," as the term is used in this paper, is defined as the ratio between the intensity of the light reflected by the paper and the intensity of the light incident upon the paper. The reflection may be diffuse or specular. "Brightness" is a more exact but a less convenient term.

³ Cf. Taylor, *Scientific Papers U. S. Bur Standards*, 405 (1920); Rhodes and Fonda, *Ind. Eng. Chem.*, 18, 130 (1926).

side, 30 cm. high). Both containers gave the same results; the use of lead caused no appreciable discoloration of the pulp. The paper was pulped with a horizontally rotating brass paddle mounted on a vertical steel shaft. The speed was about 1300 R.P.M.

Thirty to forty minutes of pulping gave a well disintegrated pulp from which uniform sheets of paper could be made. In every case pulping was begun at the temperature of the laboratory, but when the pulp was thick (50 grams paper per liter) the temperature rose 10 to 15 degrees during the process.

A special paper-making box was used in forming the sheets of paper. This consisted of a rectangular box of brass (16.8 cm. long, 10.5 cm. wide, and 6.5 cm. high) open at the top and fitted with a rectangular brass collar (of the same dimensions as the box), which however formed a separate and readily detachable part of the whole. Box and collar were held together by wing screws extending through a wide flange at the bottom of the collar and a mated flange at the top of the box, with a rubber gasket between to make a water-tight connection. A sheet of brass Fourdrinier screen supported on a perforated plate rested on the flange of the lower box and was held firmly in place by the gasket. The box was fitted with an outlet tube near the bottom, the whole apparatus forming a demountable suction-box, when assembled.

In making a sheet of paper, water was run into the box and up into the collar until the screen was just submerged. Two hundred cc. of 1 per cent pulp was then poured into the collar, and, after the pulp had been distributed evenly, the water was allowed to drain slowly from the whole apparatus. A loose felt of paper was deposited on the screen; this was drained thoroughly by suction.

The collar was then unscrewed and the screen carrying the wet paper was removed to a piece of blotting paper. A second Fourdrinier screen was placed upon the upper surface of the felt, after which the two screens carrying between them the wet paper were pressed between sheets of blotting paper. The smooth compact felt was then stripped from the screens and dried at 60°. The dried sheets were finally pressed flat in a letter-press.

The unsized and uncalendered sheets so prepared were much looser in texture than ordinary newsprint. The sheets were extremely uniform, however, in thickness, texture, and character of the surface and each was flat and free from wrinkles.

The sheets of paper now being ready, the next step was to measure their whiteness with the Taylor reflectometer. This apparatus is an integrating photometer by means of which one may measure the intensity of the light incident upon the test paper and also the intensity of the light reflected, the ratio of these two intensities being

the whiteness of the paper, in accordance with the definition formulated in an earlier paragraph.

The reflectometer is shown in Figure 1. A hollow sphere of spun copper, 12.7 cm. in diameter, was provided with three openings, A, B, and C, as shown. To one opening A, was fitted a lighting tube which could be rotated so as to direct a beam of parallel light either upon the inside of the sphere or upon the surface of the test paper placed below the opening B. The lighting tube carried a tungsten lamp (light source) together with a set of lenses and diaphragms. The telescope of a Macheth illuminometer was attached to the opening C for the purpose of measuring the intensity of illumina-

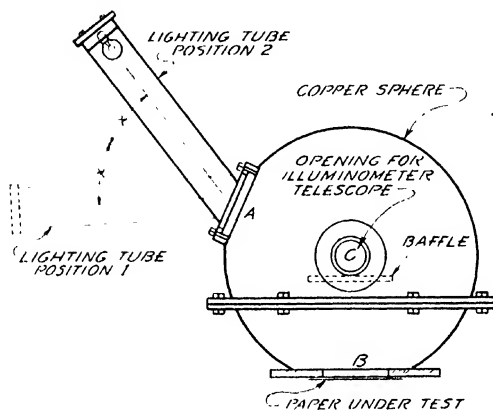


Fig. 1.

tion inside the sphere. A baffle plate was mounted inside the sphere as shown, so that light falling upon the paper could not be reflected *directly* into the telescope of the illuminometer. The baffle and the entire inner surface of the sphere were covered with a white photometer paint.

In determining whiteness the lighting tube was placed in a definite position (indicated by a stop-mark) so as to direct the beam of light upon the inner surface of the sphere (Position 1, Figure 1). The intensity of illumination inside the sphere was then measured. The lighting tube was next turned through an angle of 180° (indicated by a second stop-mark) so as to direct the beam upon the surface of the paper below B (position 2). The intensity of illumination was again measured. The last measurement divided by the first gave the whiteness of the paper.

In determining whiteness with the apparatus the only precaution necessary was to see that the current in the light-source and in the working-standard lamp of the illuminometer remained constant during the short time needed to make the two readings. Ordinarily, little difficulty was met with in this regard. At least five check determinations were made on each sheet of paper and the mean of these was taken. Under these conditions the average deviation from the mean was found to be about ± 0.005 for the individual determinations.

The Determination of the Amount of De-Inking.

The whiteness of the paper resulting from a given process of de-inking is of course a measure of the practical effectiveness of the process. Since the whiteness of the paper must be related in some way to the amount of ink retained by the paper after the process of pulping, it should be possible to determine quantitatively the extent of de-inking from the measurements of whiteness. Accordingly the following method was adopted.

Known mixtures of printed and unprinted paper were pulped as described, without any removal of ink or any discoloration of the paper fibers. Sheets of paper were prepared from these mixtures and their whiteness measured. A graded series of "de-inking standards" was thus obtained, which enabled the relation between whiteness and relative ink content to be found, and to be represented graphically by means of a curve (Cf. Figure 2).

It was not possible to use distilled water in pulping these mixtures for the reason that a surprisingly large amount of ink was removed in this way (Cf. Table II). It was found, however, that dilute solutions of acids or neutral salts could be employed in pulping, without a trace of ink being lost in the pulping liquid. Accordingly 50 grams of each mixture of printed and unprinted paper was pulped for 40 minutes in one liter of 0.02 *N* aluminum chloride and sheets were prepared as described. The whiteness of these standards is given in Part A of Table I.

At a later date a second series of standards was made from a different supply of paper as follows. Two 50 gram portions, one of printed, the other of unprinted paper were pulped in 0.1 *N* sodium chloride. Several different mixtures of printed and unprinted paper were prepared from these by combining them in the proper amounts, and these mixtures after being repulped in salt solution were made into sheets. The whiteness is recorded in Part B of Table I.

TABLE I

WHITENESS OF DE-INKING STANDARDS

Part A—Mixtures pulped in 0.02 *N* AlCl₃ or 0.02 *N* NaCl.

Unprinted Paper Per Cent	Whiteness	Unprinted Paper Per Cent	Whiteness
0.....	0.56 ₆	50	0.64 ₆
10.....	0.58 ₂	60	0.65 ₂
20.....	0.59 ₄	70	0.67 ₂
30.....	0.60 ₃	80	0.71 ₂
40.....	0.61 ₁	90	0.75 ₂
50.....	0.64 ₄	100	0.80 ₂

Part B—Mixtures pulped in 0.1 *N* NaCl

Unprinted Paper Per Cent	Whiteness	Unprinted Paper Per Cent	Whiteness
0.....	0.50 ₆	75	0.70 ₂
25.....	0.60 ₂	100	0.78 ₂
50.....	0.63 ₂	100 *	0.78–0.80

* Refers to unprinted sheet of *Phaca Journal* News, unprinted

With these data a curve was constructed (Figure 2) between whiteness as ordinates and per cent unprinted paper as abscissae. This curve is not a straight line. If we assume that the reflectometer gave correct values of whiteness, we are forced to conclude that whiteness and ink-content are not inversely proportional, though one might expect them to be so at first sight. Apparently the mixtures containing a small amount of printed paper are darker than their carbon-content would appear to require; which leads to the conclusion that the tinting strength of a small quantity of ink is relatively greater than that of a larger amount. This increased tinting strength may be due to a more complete distribution of carbon black, in smaller individual particles, over the paper fibers, and may be an illustration of the principle that tinting strength is dependent upon both the particle-size of the tinting pigment and the distribution factor.⁴

By using in the experiments on de-inking the same supply of printed paper that was utilized in preparing the standards, it was possible to read directly from the whiteness curve under discussion the per cent de-inking accomplished in the experiment, since de-inking may be expressed conveniently in terms of per cent conversion of printed paper into ink-free pulp (unprinted paper). This is true of course only when the sole action of the detergent is the removal of ink. If the fibers are bleached or discolored, or if the tinting strength of the retained ink is different from that in the standards employed in obtaining the curve, the values of de-inking read from the latter may

⁴ Cf. Briggs, *J. Phys. Chem.*, 22, 216 (1918).

be in error. As some uncertainty is at present inherent in the method, the values got from the curve will be termed in what follows the *apparent* de-inking.

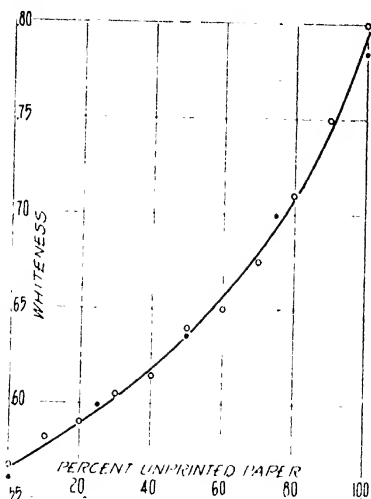


FIG. 2.

Comparison of Various De-Inking Agents.

Experiments were now carried out to compare a number of substances as to their effectiveness in de-inking. The experimental conditions were kept as nearly as possible alike throughout the series, but no special effort was made to ascertain the best conditions of operation or to reproduce those used in practice.

Fifty grams of printed paper was pulped for 30 minutes in one liter of a solution containing the detergent, the glass container being used throughout. The pulp was filtered with suction to remove most of the liquid containing the detergent and the peptized ink, and the cake of pulp was stirred into a liter of distilled water. This was again filtered. Washing and filtering were repeated at least four times, or until the filtrate became clear and free from suspended ink. The pulp was then made into sheets of paper (in dilute salt solution, to prevent the possible loss of ink in the paper-making box). The data on whiteness and apparent de-inking appear in Table II.

TABLE II
COMPARISON OF DETERGENTS

50 grams of printed paper pulped 30-40 minutes in 1 liter of solution.
Pulp washed.

Pulping Solution	Concentration	White- ness	Apparent De-Inking (Per Cent)
Sodium oleate	5 grams per liter	0.79 _s	100
Fullers' earth in 0.02 <i>N</i> NaOH	10 grams per liter	0.76 _s	95
Sodium silicate "O" Brand	0.1 <i>N</i>	0.72 _s	84
Sodium resinate	5 grams per liter	0.71 _s	83
Sodium hydroxide	0.1 <i>N</i>	0.71 _s	82
Sodium hydroxide	0.02 <i>N</i>	0.70 _s	78
Borax	0.1 <i>N</i>	0.69 _s	75
Gelatin in 0.02 <i>N</i> NaOH	10 grams per liter	0.68 _s	71
Sodium hydroxide (70°- 55°)	0.02 <i>N</i>	0.68 _s	70
Sodium carbonate	0.1 <i>N</i>	0.67 _s	69
Gum arabic	10 grams per liter	0.66 _s	65
Gelatin	10 grams per liter	0.64 _s	55
Sucrose	0.1 <i>N</i>	0.62 _s	46
Distilled water	—	0.60 _s	30
Egg albumen	10 grams per liter	0.59 _s	26
Sodium chloride	0.01 <i>N</i>	0.56 _s	0
Calcium chloride	0.01 <i>N</i>	0.56 _s	0
Aluminum chloride	0.01 <i>N</i>	0.56 _s	0
Calcium hydroxide	(saturated)	0.55 _s	0

The data of Table II allow several interesting conclusions to be drawn. Among the de-inking agents studied, sodium oleate is outstanding--which is what one might expect in view of the known detergent activity of the soaps. Sodium resinate is good, but not so effective as the oleate; free rosin appears to be adsorbed by the fibers, giving a slightly sticky feel to the pulp. The other colloids are decidedly less active--even so good a protective colloid as gelatine is comparatively a poor de-inking agent. Gum arabic appears to be fair, but it is not outstanding, although it is known to peptize carbon-black and is much used as an emulsifying agent. Egg albumen appears to be a slight anti-detergent, since less ink was removed by a one per cent solution than was removed by distilled water alone. The albumen appeared to be coagulated completely and adsorbed by the paper, since the heavy foaming that was first observed during pulping later disappeared entirely. The albumen apparently acted somewhat as a mordant does in dyeing, aiding in fixing the ink on the fibers.

A surprisingly large fraction of the ink is removed by distilled water. Tap water was tried also with about the same result. Anything which on addition to water gives a whiter paper than water alone does, may be termed a detergent or de-inking agent, provided of course the substance has no true bleaching action on the fibers,

On the other hand anything which opposes the de-inking action of water, and does not discolor the fibers, may be called an anti-detergent. The neutral salts—and the same is true of strong acids and the soluble alkaline earth metal bases—are evidently extremely powerful anti-detergents in de-inking. The non-ionized solutes such as sucrose appear to be more or less inert.

Sodium hydroxide, and the sodium salts of weak acids which are hydrolyzed in water, are effective de-inking agents. They do not appear to peptize much ink directly, as soap does, but seem to loosen the ink so that it is washed readily out of the pulp in the subsequent treatment. Thus, after pulping with sodium oleate the pulping liquid obtained on filtering was black with suspended ink, while with the alkaline de-inking agents an amber-colored pulping liquid was obtained which did not appear to carry much ink in suspension, but ink was apparently eliminated gradually during the subsequent washing of the pulp. It seems likely that the method of washing out the loosened ink from the pulped fibers is of primary importance in the case of the alkaline detergents. This point should be investigated further.

With the soaps the ink is loosened from the fibers and carried into a stable suspension of very fine particles, so removal from the pulp is easy. With sodium hydroxide, however, a stable suspension of fine ink particles is not formed and some method of collecting the partly peptized or loosened ink is needed. At first sight the addition of gelatine to the base might be expected to stabilize the suspension. The experiment was tried but failed, as the data of the table indicate. Florida fullers' earth, on the other hand, produced the desired effect, acting as a collecting agent. It is believed that the fullers' earth adsorbed the ink and this complex in turn was peptized readily by sodium hydroxide. Indeed the combination of fullers' earth and alkali was almost as effective as soap.⁵

The alkaline detergents, however, have the disadvantage of discoloring the pulp in the case of mechanical wood-pulp, turning the latter somewhat yellow. This effect increases with the concentration of the free alkali. This discoloration causes the values of whiteness to be too low, as measured in the reflectometer. It was found, however, that the yellow color could be discharged by acidifying the pulp with a few drops of concentrated hydrochloric acid, the latter being added just before the preparation of the sheets of paper for the measurement of whiteness.

In one particular experiment with 0.1 *N* sodium hydroxide the whiteness of the paper before treatment with acid was 0.69, after the treatment with acid this rose to 0.71. Some yellowing was also observed

⁵In this connection cf. Baskerville and Stevenson, *loc. cit.*, *J. Ind. Eng. Chem.*, **13**, 218 (1921); Wells, *Paper*, 30, 7 (1922).

with sodium silicate, sodium carbonate and borax. In obtaining the data given in Table II for the alkaline detergents, the yellow discoloration was removed in every case by the addition of dilute hydrochloric acid to the pulp after washing.

In one experiment the paper was pulped in a hot solution of sodium hydroxide instead of a cold one (Cf. Table II). No improvement in de-inking was noted—if anything, a decreased detergent effect resulted.⁶

The quantity of neutral salt necessary to prevent any removal of ink on pulping was found to be very small. A perfectly clear pulping liquid was obtained with 0.001 *N* solutions of AlCl_3 , CaCl_2 or MgCl_2 . With 0.001 *N* NaCl the pulping liquid was slightly dark with suspended ink, this was decidedly the case with 0.01 *N* sodium citrate. The anti-detergent action of the salts appears to follow the order: AlCl_3 , CaCl_2 , $\text{MgCl}_2 > \text{NaCl} > \text{Na Citrate}$. Hydrochloric and sulfuric acids in dilute solution showed a similar anti-detergent action, but citric acid did not. Apparently adsorbed cations oppose de-inking while adsorbed anions favor it.

The de-inking obtained with sodium oleate solutions of different concentrations was next investigated, the procedure of the previous experiments being employed. The data follow (Table III).

TABLE III
DE-INKING WITH SODIUM OLEATE

Grams Sodium Oleate per Liter	Whiteness	Apparent De-Inking (Per Cent)
0.....	0.60 _s	32
1.....	0.68 _a	73
5.....	0.79 _a	100
10.....	0.80 _a	100
20.....	0.79 _a	100
50.....	0.79 _a	99
100.....	0.77 _a	97

There is apparently no particular intermediate concentration of soap giving a pronounced maximum de-inking effect, though a slight optimum seems to exist at a concentration of about 10 grams per liter. Such a point of optimum de-inking might be expected in view of the results of McBain, Harborne and King⁷ and of Fall,⁸ who found a decided concentration-optimum in the peptizing power of soap.

A similar series of experiments was carried out with sodium hydroxide. In this series, however, a more dilute pulp was employed,

⁶ A similar decrease in the detergent action of soaps with rise of temperature has been observed by McBain and confirmed by Fall in this laboratory. Cf. McBain, Harborne and King, *J. Phys. Chem.*, **28**, 1 (1924); Fall, Cornell Univ. Thesis, "The Detergent Action of Soaps," 161 (1925).

⁷ Loc. cit., *J. Phys. Chem.*, **28**, 1 (1924).

⁸ Fall, loc. cit., p. 147.

10 grams of printed paper being pulped in 900 cc. of the detergent solution. Since it was found that de-inking is generally more complete in a dilute pulp than in a concentrated one, the results obtained in the present series are not comparable directly with those appearing in Tables II and III.

After pulping for 30 minutes, the pulp was diluted to one liter and two sheets of paper were made directly from this pulp, without submitting the latter to the usual process of washing. The remaining pulp was then filtered, washed, squeezed, and repulped in enough water to restore the pulp to its original composition (10 grams per liter), after which sheets of paper were prepared as before. In this series of experiments no hydrochloric acid was added to remove the yellow color, so that the whiteness data represent the results got with sodium hydroxide alone and do not necessarily measure the actual de-inking accomplished. The data follow (Table IV).

TABLE IV
DE-INKING WITH SODIUM HYDROXIDE

10 grams printed paper pulped in 900 cc. for 30 minutes

NaOH	Sheets Prepared	Color	Whiteness	
			Top	Bottom
0.5 N	From original pulp	Yellowish	0.67 ₂	0.59 ₂
0.5 N	After repulping in H ₂ O	"	0.62 ₂	0.59 ₂
0.1 N	From original pulp	Slightly yellowish	0.74 ₂	0.70 ₂
0.1 N	After repulping in H ₂ O	Slightly yellowish	0.74 ₂	0.74 ₂
0.02 N	From original pulp	Almost no yellow	0.78 ₂	0.72 ₂
0.02 N	After repulping in H ₂ O	Almost no yellow	0.75 ₂	0.74 ₂
0.01 N	From original pulp	No yellow	0.69 ₂	0.66 ₂
0.01 N	After repulping in H ₂ O	" "	0.67 ₂	0.67 ₂

It appears from these experiments that the greatest whiteness is obtained when the sodium hydroxide lies approximately within the limits of 0.1 and 0.02 normal. This conclusion is an interesting confirmation of the statement by Berl and Pfannmüller⁹ who recommend in de-inking N/20 to N/60 solutions of sodium hydroxide, together with tetralin to collect the ink. It is also evident that the yellow discoloration of the fibers becomes excessive as the concentration exceeds the upper of these two limits.

In Table IV it is apparent that the limiting minimum concentration of sodium hydroxide lies between 0.02 and 0.01 normal. With a larger amount of paper—50 grams instead of 10 grams—the limiting minimum

⁹ *Loc. cit.*, *Z. angew. Chem.*, **39**, 887 (1925).

concentration was found to lie between 0.04 and 0.02 normal. This difference is apparently the result of adsorption of sodium hydroxide by the fibers of the pulp, for the actual concentration of base in the pulping solution is the factor which really determines the whiteness of the pulp. The amount of sodium hydroxide adsorbed by the paper was therefore determined (Table V).

TABLE V
ADSORPTION OF NaOH DURING PULPING

Paper pulped 30 minutes in 1 liter of solution.

Grams of Paper Pulped	Original Concentration of Pulping Solution, Moles NaOH per Liter	Final Concentration of Pulping Solution, Moles NaOH per Liter	Moles NaOH Adsorbed
10.	0.1000	0.0956	0.0044
50	0.1005	0.0806	0.0199
50	0.0400	0.0252	0.0148
50	0.0295	0.0185	0.0110
10	0.0199	0.0113	0.0025
50	0.0199	0.0174	0.0086

The data of Table V show that the limiting minimum concentration of sodium hydroxide for effective de-inking is approximately 0.02 normal, both for the concentrated and the dilute pulp, provided the concentration of the solution actually in equilibrium with the fibers is referred to.

Some unusually interesting relations were discovered on studying different methods of carrying out the treatment with sodium hydroxide, in which the order of adding the alkali was varied. Runs were made as follows: 50 grams of paper was pulped for 30 minutes with 0.02 *N* NaOH as usual. Next a second run was made, the paper being pulped for 30 minutes in distilled water before adding the alkali. The alkali was then added directly to the water and the whole was pulped 30 minutes longer. A third run like the last was also made, with the difference that the paper was filtered off, washed, and dried after pulping in water; the dried pulp was then repulped in sodium hydroxide for 30 minutes as usual. The results appear in Table VI, several check runs being included.

Pulping the paper in water, before the addition of the detergent (NaOH) has evidently a powerful retarding action upon de-inking. It appears to render the alkali almost inactive. This peculiar effect is probably caused by a redistribution of the ink on the fibers, taking place during the preliminary disintegration in water, and tending to increase the adherence of the carbon-black to the fibers, so that de-inking is made exceedingly difficult. This explanation is plausible and is in

TABLE VI
 DE-INKING, WITH NaOH—EFFECT OF PREVIOUS PULPING IN WATER

(50 grams paper in one liter, 0.02 N NaOH, pulp acidified with HCl before making sheets)	Whiteness			Apparent De Inking		
	a *	b †	c †	a *	b †	c †
(1) Pulped directly with NaOH, 30 min.	0.71,	0.70,	0.70,	82	77	77
(2) Pulped 30 min. in H ₂ O, then 30 min. in NaOH.	0.63,	0.62,	0.63,	50	42	50
(3) Pulped 30 min. in H ₂ O, pulp dried, then repulped 30 min. in NaOH.	0.62,	—	—	41	—	—
(4) Pulped 30 min. in H ₂ O, no NaOH.	0.60,	0.60,	0.60,	32	30	31
(5) No. 1(b) above, repulped 30 min. in H ₂ O after washing out NaOH.	—	0.69,	—	—	76	—

* Pulped in lead jar † Pulped in glass jar

accord with the observations of Baskerville and Joyce,¹⁰ who have pointed out that excessive pulping imbeds the ink into the fibers in such a way as to render its subsequent removal impossible, and who accordingly recommend the mildest possible treatment of the paper in practice.

With sodium oleate the anti-detergent effect of previous pulping was similar, but less pronounced. Direct pulping in 0.5 per cent soap solution gave a whiteness of 0.79, corresponding to complete de-inking. Following previous pulping in water, the same solution gave 0.74, or 91 per cent de-inking.

The following experiment was performed to determine whether or not the ink left in the paper after a previous treatment with alkali could be taken out by a second treatment with the same detergent. Fifty grams of paper was pulped in 900 cc. of 0.03 N NaOH. The whiteness of the sheets (not bleached with HCl) was 0.69. The remainder of the pulp was squeezed dry and then re-pulped in 1000 cc. of alkali solution of the same concentration as the filtrate from the original pulping. Since the whiteness of the paper resulting from the second treatment was found to be 0.68, it is evident that none of the retained ink was taken out.

Special experiments¹¹ were carried out with a number of the other detergents. In a series with sodium carbonate 10 grams of paper was pulped with 900 cc. of the solution for 30 minutes. The pulp was washed and then repulped in dilute salt solution before preparing the sheets of paper. 0.2, 0.1, and 0.02 normal solutions gave 0.67, 0.68, and 0.70, respectively, as the values of whiteness, a slight yellow dis-

¹⁰ *Loc. cit.*, *J. Ind. Eng. Chem.*, **13**, 214 (1921); Joyce, *Met. Chem. Eng.*, **25**, 242 (1921)

¹¹ Performed by Mr. A. S. Jarecki, as part of his Senior research.

coloration of the fibers occurring only with the most concentrated solution. When ammonium hydroxide was tried as de-inking agent, with 1.0, 0.1 and 0.02 normal solutions, the results were 0.51₈, 0.58₆, and 0.65₇, respectively. With the strong solution of ammonium hydroxide the discoloration of the fibers is evidently quite extreme, for the paper was much less white than was paper pulped in salt solution, in which the ink is completely retained (compare 0.51₈ with 0.56₇, the value for 0.02 *N* NaCl, given in Table II). Trisodium phosphate was found to be about as effective a de-inking agent as sodium hydroxide, which is quite as one would expect it to be.

A careful study of different kinds of "sodium silicate" was also made, for the purpose of finding out whether the presence of excess silica has any special effect on de-inking. Three brands of silicate of soda were supplied by the Philadelphia Quartz Co., marked "S," "O," and "C," in which the SiO₂:Na₂O ratios were 3.89, and 3.23 and 2.00 respectively, as determined by analysis. Ten grams of printed paper was pulped for 30 minutes as usual, the pulp was washed, and sheets were made. The results appear in Table VII.

TABLE VII
DE-INKING WITH SODIUM SILICATE

10 grams paper pulped 30 minutes. Pulp washed in water.			
Concentration Equivalents Na ₂ O per Liter	"S" Brand SiO ₂ : Na ₂ O = 3.89	"O" Brand SiO ₂ : Na ₂ O = 3.23	"C" Brand SiO ₂ : Na ₂ O = 2.0
0.2	0.69 ₈	—	0.63 ₆
0.1	0.73 ₆	0.72 ₃	0.70 ₆
0.05	0.71 ₁	0.71 ₂	—
0.02	0.69 ₈	0.69 ₈	0.69 ₈

The de-inking accomplished by the "S" brand, in which the silica ratio is the highest, may possibly be the best, but the advantage, if real, is very slight. Apparently the excess of silica, present as a sol in the pulping solution is unable to exert to a marked degree any intrinsic detergent action.¹² Sodium silicate is a good de-inking agent, but there is no evidence that it is superior to sodium hydroxide.

A number of other possible de-inking agents have also been investigated in the course of this work, but as the procedure was not controlled with the necessary precision, the data have not been included in the various tables. Among the colloids, sodium protalbinat and lysalbinat, sodium caseinate, saponin, and a solution of licorice extract were found relatively ineffective. The same is true of a saturated solution of amyl alcohol.

¹² Cf. Fall, *loc. cit.*, p. 171.

A Quantitative Method of Measuring Detergent Action

Many methods,¹³ mostly qualitative and indirect, have been proposed for the measurement of detergent action. The best of these is probably the method developed by McBain and his co-workers¹⁴ and improved by Fall¹⁵ in this laboratory. Fall ascertained how much finely-divided manganese dioxide (specially prepared by grinding in a colloid-mill) could be kept in suspension for a definite time by the various detergents, using a particular experimental procedure. This gave him a "MnO₂ value" which was supposed to measure the detergent value of the material used. In McBain's method a so-called "carbon value" was determined in somewhat the same way.

It is an open question whether peptization methods of this sort really measure the effectiveness of a detergent in any actual process of washing, such as de-inking is. Attempts to measure detergent power by direct washing tests have therefore been made,¹⁶ but not with great success. Stericker carried out a few tests with soiled mechanics' overalls and concluded that sodium silicate Na₂O.3SiO₂ possessed some real detergent action. Zhukov and Shestakov washed specially soiled cotton and concluded that olein soaps were superior to rosin soaps, but no details of their procedure were given. Heermann washed specially soiled goods and compared the whiteness of the product with a set of "standards" much as we have done in the present work on de-inking. Comparison was made with the naked eye, however, and could not have been very accurate or trustworthy.

It is believed that the technique developed during the present investigation of de-inking can be employed in measuring detergent power by direct washing tests. That the data of Table II represent a fairly accurate evaluation of the absolute detergent power of various de-inking agents, has been pointed out in the preceding discussion. The printed paper serves as the soiled material. The unprinted paper is the standard by which perfect cleaning can be determined. The use of the Taylor reflectometer enables accurate quantitative measurements to be made. The weak point in the method as developed so far lies however in the tendency of mechanical wood-pulp to be discolored, especially in alkaline solutions. With printed book-stock this would not be so serious a problem. At any rate, the method is promising and it will be tested thoroughly in the near future.

¹³ Cf. summary by McBain, Third Colloids Report, Brit. Assoc. Adv. of Science (1920).

¹⁴ Cf. McBain, Harborne and King, *loc. cit.*, *J. Phys. Chem.*, **28**, 1 (1924).

¹⁵ Fall, *loc. cit.*, Cornell Univ. Thesis (1925).

¹⁶ Zhukov and Shestakov, *Chem. Ztg.*, **35**, 1027 (1911); Stericker, *Ind. Eng. Chem.*, **15**, 244 (1923); Heermann, *Z. deut. Öl-Fett Ind.*, **44**, 361, 378, 391 (1924); *Chem. Abstr.*, **18**, 3485 (1924).

Summary.

The results of this paper may be summarized as follows:

1. A laboratory method for the quantitative study of de-inking has been described and a preliminary report on the results obtained has been made.

2. Printed newsprint is pulped in a solution of the detergent, the loosened and peptized ink is removed by washing, and the pulp is converted into test sheets of paper. The whiteness of these test sheets is then measured with a Taylor reflectometer. This value of whiteness is used to determine the degree of de-inking, by comparison with the whiteness of known mixtures of printed and unprinted paper.

3. Soap (sodium oleate) effects the greatest de-inking, the latter being complete between the concentrations of 0.5 and 5 per cent. Rosin soap (sodium resinate) is less effective.

4. Alkaline solutions in general are active de-inking agents. Fullers' earth increases the detergent power of sodium hydroxide, and gives almost as much de-inking as soap. With sodium hydroxide maximum de-inking occurs between the limits of 0.1 and 0.02 moles per liter.

5. Water alone, without any special detergent, removes a large amount of ink. But the strong acids, the neutral ionized salts (especially those with polyvalent cations), and the alkaline-earth metal hydroxides are anti-detergents, preventing any de-inking by water whatsoever.

6. Typical protective colloids, such as gum arabic or gelatin, prove to be comparatively ineffective de-inking agents.

7. The de-inking power of sodium silicate is not greatly affected by the $\text{Na}_2\text{O} : \text{SiO}_2$ ratio.

8. Rise of temperature appears not to increase de-inking power.

9. If paper is pulped in water previous to the de-inking treatment, the removal of ink becomes much more difficult. The ink is ground into, and retained firmly by, the fibers.

10. In the case of soap the ink is loosened from the fibers and suspended permanently in the soap solution so that removal from the pulp is easy. With the alkaline detergents the ink is loosened but not suspended, so that special methods have to be employed in collecting and removing the ink. This may be done mechanically by washing the pulp in a rapid stream of water, by adding a collecting agent such as an oil, or by the use of a finely divided solid in suspension (fullers' earth) which adsorbs the ink and carries it into suspension.

11. The ideal de-inking agent is probably some substance, preferably a colloid, which is adsorbed much more strongly by ink than by paper, and tends to peptize ink. If the substance is a colloid and is adsorbed

more strongly by paper than by ink, a mordanting action results, which tends to bind the ink to the fiber. Such an effect has been observed with albumin.

12. If the theory outlined in the last paragraph is correct, detergent power cannot be evaluated by peptization measurements alone (methods of McBain and Fall). The present technique, as applied to de-inking, is offered as a promising method of measuring detergent power.

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THE SO-CALLED ADSORPTION OF FERRIC OXIDE HYDROSOL BY CHARCOAL

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While the literature discloses many investigations on the adsorption of "Crystalloidal" electrolytes and non-electrolytes by various charcoals, yet the adsorption of inorganic colloidal dispersions by charcoal has received but slight attention. Nils Carli¹ made some experiments in 1913 on the adsorption of iron oxide sol by charcoal. He refers in his report to some previous experiments by Freundlich and Losev, stating that these investigators had found that charcoal has no appreciable adsorptive power for iron oxide sol, but that no quantitative data was given. The reference cited for this work is not available, and furthermore, Freundlich, in his "Kapillarchemie" makes no reference to the subject.

In his experiments, Carli used an iron oxide sol obtained from Kahlbaum, and a charcoal "*Carbo animalis purissimus P. A.*" supplied by Merck. He stated that he found this charcoal had practically the same adsorbing power on iron oxide sol as that of a specially acid purified and washed charcoal prepared in his laboratory. His test for soluble impurities in the Merck's charcoal consisted in shaking two grams with distilled water for three hours, after which the sample was let stand over night. Chemical tests for chloride and sulphate ions in the supernatant liquid were negative.

As a result of his experiments, Carli came to the conclusions (1) an appreciable adsorption existed between animal charcoal and colloidal iron hydroxide. (2) Within the limits of the investigation region, the adsorption was directly proportional to the quantity of charcoal. (3) The adsorption was independent of the volume of the solution, and of the quantity of colloid present in the solution; i.e., the concentration.

Carli's experimental results showed that when using the same quantity of charcoal and varying concentrations of the iron oxide sol, complete removal was obtained up to a certain concentration after which the amount of iron oxide adsorbed remained constant, the average value being 0.129 gram iron hydroxide per gram charcoal. These findings indicated that the study of adsorption of inorganic colloidal dispersions by various adsorbents, might yield interesting experimental results.

¹ *Z. physik. Chem.*, 85, 263 72 (1913).

It was first attempted to duplicate the results of Carli. To this end iron oxide sols of varying purity were treated with highly purified Norite charcoal. The test experiments were filtered through S. and S. paper #590 (following the example of Carli) and the difference in concentration between the original sol and the filtered sol was considered the quantity that had been adsorbed by the charcoal. An apparent adsorption was obtained, but the values for the same were very irregular—giving curves of a definite trend but irregular in their parts.

Due to the extreme slowness with which the sol passed through the on-lying bed of charcoal and filter paper, it was decided to try centrifuging, taking the aliquot for analysis from the supernatant liquid. This change was effective, and upon making the next test for adsorption, it was found that the supernatant liquid contained the same concentration of iron as the original sol. This was confirmed by several repetitions at different time intervals. Hence it was concluded that the adsorption previously found could not be attributed to charcoal alone, but that the filter paper might be involved.

The sorptive² properties of filter paper are well known.³

Method of Investigation.

The results of the above described tests made it clear that in these sorption tests it would be necessary to use the centrifuge in separating the adsorbent from the solution of the adsorbate.

In general, the procedure observed was as follows: Usually one gram of a given charcoal was weighed and transferred to a 250 cc. Non-Sol glass stoppered bottle. To this, 100 cc. of the sol or solution under test was added. The bottle was then turned in a rotating machine for the required period of time, when the contents were transferred to a centrifuge tube and centrifuged about ten minutes. An aliquot of 50 cc. of the clear supernatant liquid was transferred to a beaker to which 25 cc. of a 3.8 molar sulphuric acid solution were added, after which the liquid was evaporated on a hot plate to white sulphur trioxide fumes, at which point it was assumed all halide had been removed. After cooling, about 100 cc. of water were added, and the contents heated to boiling. The beaker was now removed and allowed to cool to room temperature. It was poured through a Jones reductor, and the iron determined by titration with N/10 potassium permanganate which had been standardized against Bureau of Standards sodium oxalate. The difference between the concentration of iron expressed as Fe_2O_3 per 100 cc. before and after such a test was considered the amount of iron expressed as Fe_2O_3 sorbed by the charcoal.

² Since the removal of substances from solution by solid "adsorbents" is not always adsorption according to the strict meaning of this term, the word *sorption* will be used throughout this discussion.

³ Spring, *Kolloid-Z.*, **6**, 11, 109, 164 (1909); Evans, *J. Phys. Chem.*, **10**, 290 (1906); Murray, *J. Phys. Chem.*, **20**, 621 (1916), Leighton, *J. Phys. Chem.*, **20**, 188 (1916).

Preparation and Purification of Materials Used:**Preparation of Iron Oxide Sols.**

A given volume of a 2.7 molar ferric chloride solution was diluted with an equal volume of water, and to this was added approximately 10 molar ammonia solution, drop by drop, with constant stirring until the precipitated flocks of hydrous ferric oxide re-dissolved with difficulty. The mass was dialyzed in collodion bags in running tap water for from 4 to 8 hours, after which the tap water in the dialysis jars was replaced by distilled water. Early in the dialyzing period, the distilled water was replaced at least twice each day, while later, the water was replaced only once per day. Since it was desired to obtain a series of sols of graded Fe/Cl ratio, the contents of the several dialysis bags were united, and a definite fraction was removed at certain intervals of time, say 9, 17, 23 days. The removed sol was bottled and reserved for analysis and use. With this concentrated sol of known Fe/Cl ratio, it was then possible by dilution, to obtain any desired concentration of the sol with a known Fe/Cl ratio.

The residue of the sol was returned to fresh collodion bags, and dialysis continued.

Analysis of the various sols follows: The numbers given the sols, have the following significance, e.g., 4-9 is 4th batch of sols, and this is the fraction removed after 9 days of dialysis.

The iron content was determined by the method already described. The chlorine content was determined either gravimetrically as silver chloride, or volumetrically by the Volhard titration.

TABLE I
IRON OXIDE SOLS

No.	Designation	Fe/liter gram-atoms	Cl/liter grams-atoms	"Purity"
				$\frac{\text{Equiv. Fe}}{\text{Equiv. Cl}}$
1.....	4-9	0.2050	0.0343	17.9
2.....	3-7	0.2165	0.0337	19.3
3.....	4-14	0.1620	0.0224	21.7
4.....	3-17	0.1751	0.0206	25.6
5.....	32-14*	0.1431	0.0146	29.4
6.....	3-23	0.1225	0.0119	30.9
7.....	(32-14)32†	0.1312	0.0105	37.5
8.....	2-32	0.1214	0.0075	48.6

* Prepared by mixing equal volumes of 8 and 3 and allowed to stand 10 days before use.

† Prepared by mixing 1.5 parts by volume of 8 and 1.0 part by volume of 5, and allowed to stand 10 days before use.

Charcoals.

Five different charcoals were used in these experiments, comprising the three types: vegetable, animal and sugar.

Their characteristics and purification are listed below. The data

on ash and acetic acid adsorptive powers are given in Table II and Figure I.

Technical Norite: Used as delivered commercially.

Blood Charcoal: Not purified. Used as delivered by chemical supply firm.

Sugar Charcoal. (From cane sugar.) Used as purchased from a chemical supply firm, except that it was ground to pass a 70 mesh sieve.

Purified Norite. A quantity of technical Norite was covered with 6 molar hydrochloric acid and then heated to about 80° C. After standing about a week at room temperature, the mass was transferred to an extraction column provided with a linen filtering membrane at the bottom, and the hydrochloric acid solution drawn through completely with the aid of suction. Distilled water was added, and after some time, drawn out with complete evacuation as before. The charcoal was repeatedly washed with distilled water until a sample, upon being withdrawn, treated with dilute sulphuric acid and filtered, gave only a very faint test for chloride ion. This washing process required about 10 weeks.

The charcoal was now transferred in the barely moist condition to a large Pyrex flask and dried in an electric oven at 105° C. for about two days, after which the flask was heated to an average of about 150° C. in a sand bath for about 10 hours under reduced pressure (vacuum pump). Upon cooling, the charcoal was spread out in glass crystallizing dishes and allowed to come into moisture-equilibrium with the outside air. The portion passing 70 mesh and retained by 200 mesh was used in the experiments.

Purified Bone Charcoal: "C.P. animal Charcoal" purchased from a chemical supply firm was purified in the same manner as described under *Purified Norite*. Since the sample consisted in the main of very fine particles, it was passed through a 100 mesh sieve and that portion retained on the sieve was used in the experiments. This amounted to about 100 grams out of a total of 500 grams.

The reaction of the water soluble extract was determined by suspending one gram of charcoal in 100 cc. of distilled water in a previously steamed Non-Sol bottle. At the end of twenty days the pH values of these aqueous extracts were:

Technical Norite	9.58
Purified Norite	4.87
Blood Charcoal	7.66
Sugar Charcoal	6.34
Purified Bone Charcoal	4.92

In view of the great diversity in the purities of charcoals used by various investigators, as disclosed by the literature on charcoal adsorption, it was considered desirable to establish more satisfactorily the degree of purity of the purified Norite and purified animal charcoal.

For this purpose, gold sols were obtained through the kindness of Mr. J. H. Young. These sols were prepared by Messrs. F. Low and G. F. Rugar, who are engaged in research on gold sols under Professor H. T. Beans.

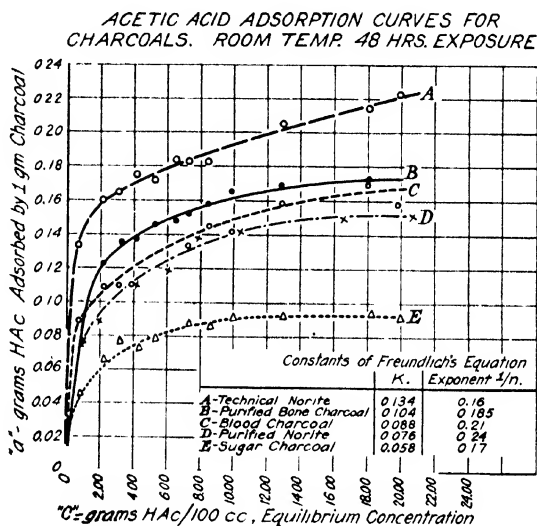


FIG 1

The description of the sols and the tests applied follows:

- Gold Sol No. 1. Bredig sol. Alternating current. KCl electrolyte. 0.0638 gms. Au per 100 cc.
- Gold Sol No. 2. Bredig sol. Direct current. 0.001 M. NaCl electrolyte. 0.0592 gms. Au per 100 cc.
- Gold Sol No. 3. Bredig sol. Direct current. 0.001 M. NaCl electrolyte. About 0.02 gms. Au per 100 cc.
- Test No. 1. 100 cc of gold sol No. 1 were treated with 0.5000 gms. of Purified Bone Charcoal. Exposure was continued six days with frequent agitation. 50 cc. of the supernatant sol were analyzed. The content of gold was found to be 0.0650 gms. Au per 100 cc. The sol had not even a suspicion of a purple color.
- Test No. 2. 100 cc. of gold sol No. 2 were treated with 0.5000 gms. of Purified Norite. Exposure was continued six days with frequent agitation. At the end of this time, the content of gold was found to be 0.0582 gms. Au per 100 cc. The color of the sol had not changed.
- Test No. 3. About 50 cc. of gold sol No. 3 were treated with 0.5000 gms. of "C. P. Animal Charcoal" (purchased from a chemical supply firm). In a few minutes the color of the sol, which was originally reddish purple, began to go through changes of color, becoming more blue. By next morning, the sol had been completely precipitated, and the liquid was water white.

TABLE II
CHARACTERISTICS OF ASH OF CHARCOALS. 5 GMS ASHED IN PLATINUM DISHES IN MUFFLE FURNACE

	Color of Ash	Reaction of Aq. Extract of Ash to	Components of the Ash (Per Cent of Total Ash)			
			(1) Water Soluble Portion	(2) HCl Soluble Portion	(3) HCl Insoluble Portion	(4) Loss on Ignition of (3) with HF.
			Per Cent of Total Ash	Per Cent of Total Ash	Per Cent of Total Ash	Per Cent of Total Ash
			Elements Identified	Elements Identified	Elements Identified	
			SO ₄ (trace)	PO ₄ Fe	PO ₄ Fe	81.2
			SO ₄ (trace)	PO ₄ Fe	PO ₄ Fe	66.9
			SO ₄ (trace) K, Na ?	PO ₄ Fe	PO ₄ Fe	30.1
			SO ₄ Cl K Na CO ₃	PO ₄ Fe Ca	PO ₄ Fe Ca	11.0
			SO ₄ Cl K, Fe Na	PO ₄ Fe Ca SiO ₂	PO ₄ Fe Ca SiO ₂	16.9

* Alkalinity, expressed as Na₂CO₃ = 6.1 per cent of total ash. (M.O. indicator.)

Discussion of Errors.

An error in titration, of variable importance, probably entered into most of the analyses. Probably, for average differences in the conditions under which the successive titrations are made, the average total error, after calculation to 100 cc., amounts to from 0.0005 to 0.0010 grams Fe_2O_3 . This is a plus-minus error, and is considered to be the most important one entering into the analyses.

Very pure iron oxide sol exhibited a tendency to cling to glass, possibly due to superficial precipitation by alkali. This was noticed more particularly in sols of high concentration and very high purity. Since the diluted sols used in the sorption tests were, with the exception of sol #8, not of an extreme purity, there was no visible evidence of such a surface effect. After a sol has been treated with a charcoal, its purity will have increased due to the removal of at least some hydrochloric acid. Therefore any error arising from this source would be a plus error, i.e., it would increase the apparent sorption.

In quite a number of instances centrifuging did not remove completely a very fine charcoal suspension from the iron oxide sol. This charcoal occupied a definite volume, causing the aliquot for analysis to contain slightly less total iron than it should. It is believed that in no case did this error exceed 0.2 cc., which for a sol containing 0.18 gram Fe_2O_3 per 100 cc. would entail a maximum plus error of 0.0004 gram Fe_2O_3 .

Tests of Sorption of Iron Oxide Sol by Various Charcoals.

A series of eight dilutions were made of three sols, one very "impure," one of average "purity," and one of high "purity," namely: sols #1, #5, and #7.

The concentrations of these diluted sols ranged from 0.232 gram Fe_2O_3 /liter to 2.759 grams Fe_2O_3 /liter.

Portions of one gram of the charcoals were treated in glass stoppered Non-Sol bottles with 100 cc. of the sol. Contact was maintained 5 days, during which the bottles were rotated at least 12 hours, and agitated at intervals during the remainder of the period.

After centrifuging, 50 cc. aliquots were withdrawn from the supernatant sol, and analyzed for total iron content, calculated in terms of Fe_2O_3 per 100 cc.

The results are tabulated in Tables III to V.

TABLE III

SORPTION OF FERRIC OXIDE HYDROSOL No. 1 BY VARIOUS CHARCOALS

$\frac{\text{Fe}}{\text{Cl}} = 17.9$	Purified Norite	Purified Bone Charcoal	Sugar Charcoal
$\text{Fe}_2\text{O}_3/100 \text{ cc.}$	Fe_2O_3	Fe_2O_3	Fe_2O_3
mgs.	sorbed mgs. *	sorbed mgs. *	sorbed mgs. *
36.6	1.8	0.0	0.5
68.4	1.6	0.2	1.3
106.1	1.8	0.5	0.1
128.0	1.6	0.3	1.6
165.1	1.3	1.4	0.2
208.8	2.3	0.6	1.0
240.9	1.3	0.0	0.3
275.9	0.7	0.9	0.5

TABLE IV

SORPTION OF FERRIC OXIDE HYDROSOL No. 5 BY VARIOUS CHARCOALS

$\frac{\text{Fe}}{\text{Cl}} = 29.4$	Purified Norite	Purified Bone Charcoal	Sugar Charcoal
$\text{Fe}_2\text{O}_3/100 \text{ cc.}$	Fe_2O_3	Fe_2O_3	Fe_2O_3
mgs.	sorbed mgs. *	sorbed mgs. *	sorbed mgs. *
29.6	0.5	0.4	1.2
60.1	1.8	0.0	1.0
81.9	1.0	1.4	1.3
117.6	1.3	1.2	1.0
148.8	0.3	1.3	0.0
178.4	2.3	0.5	1.3
201.0	2.0	1.1	0.2
228.6	0.0	2.3	0.6

TABLE V

SORPTION OF FERRIC OXIDE HYDROSOL No. 7 BY VARIOUS CHARCOALS

$\frac{\text{Fe}}{\text{Cl}} = 37.5$	Purified Norite	Purified Bone Charcoal	Sugar Charcoal
$\text{Fe}_2\text{O}_3/100 \text{ cc.}$	Fe_2O_3	Fe_2O_3	Fe_2O_3
mgs.	sorbed mgs. *	sorbed mgs. *	sorbed mgs. *
23.2	0.7	1.2	0.1
33.2	0.9	0.4	1.2
59.1	0.8	0.8	1.2
73.9	0.0	1.3	1.5
102.8	0.1	1.3	1.8
117.5	0.8	1.6	0.3
153.0	0.5	1.5	1.2
181.2	1.6	1.2	1.2

* Difference between the original concentration and the equilibrium concentration.

Considering about 1 milligram of Fe_2O_3 per 100 cc. to be the experimental error in these tests, it is apparent that highly purified charcoals

have no sorptive capacity for iron oxide sol within a period of exposure of 5 days.

In order to find whether exposure of the iron oxide sol to purified charcoal for a longer period of time would give positive sorption, the following experiment was made.

Iron oxide sol #8, $\text{Fe/Cl} = 48.6$, a sol that is so highly dialyzed that it is extremely easily precipitated by electrolytes, was diluted to a convenient strength and 100 cc. portions run into a series of Non-Sol bottles to which exactly 1 gram portions of purified Norite had been added. Two blanks were run without charcoal.

The results obtained are shown in Table VI.

TABLE VI
EFFECT OF TIME ON SORPTION OF FERRIC OXIDE HYDROSOL

Period of exposure... ..days	4	6	8	13	20	27	36
Fe_2O_3 adsorbedmgs.	1.5	1.6	1.2	-0.3	1.6	1.3	-1.5

Since in all the experiments here given, the ratio of one gram of charcoal per 100 cc. of sol was always used, and in view of the fact that Carli used a ratio of charcoal as high as two grams per 20 cc., it was considered advisable to test the effect, if any, of variable ratios of charcoal. Table VII gives the results of these tests, which were run for a period of twenty-four hours, and in which sol #5 (diluted) was used.

TABLE VII
EFFECT OF AMOUNT OF CHARCOAL ON SORPTION OF FERRIC OXIDE HYDROSOL

Purified Bone Charcoal treated with 50 cc. sol.....gms.	0.5	1.5	2.0	2.5	3.0
Fe_2O_3 adsorbedmgs.	-3.1	-1.1	-2.7	-0.8	-5.0

Still higher ratios of charcoal were used, but it was found extremely difficult to centrifuge out the charcoal, so that the analytical data obtained was meaningless. These results indicate a negative sorption, and in view of the experiments cited previously, an absence of positive sorption by purified charcoals, even when the mass of charcoal used is relatively great.

Action of Technical Norite on Iron Oxide Sols:

With these apparently wholly negative results for sorption of iron oxide sols by purified charcoals and by sugar charcoal, it became of interest to determine the character of sorption, if any, by ordinary technical, or unpurified charcoals.

Preliminary tests indicated rather high precipitative power by both

technical Norite as well as by blood charcoal. In these preliminary tests, quite outstanding results were obtained with the weak concentrations of the sol,—the sol flocculating, and settling out, with a clear water white supernatant liquid. The weaker the sol, the more rapid was this action. The flocculation and settling out taking place in periods of time varying from 10 minutes to 24 hours.

In those tests in which there was not a complete precipitation of the sol, so far as observation went, there had been no change in the sol, but later quantitative data make it appear that at least in the case of the technical Norite, these sols must have changed in constitution, probably becoming "more pure," i.e., the ratio of Fe/Cl becoming greater, due to removal of hydrochloric acid in hydrolytic or other equilibrium with the ferric oxide sol micelles.

It should be explicitly stated that when the technical charcoal causes the complete flocculation of an iron oxide sol, the action involved is not adsorption. The iron oxide flocks settle out with their characteristic brick color on, over and between the charcoal particles, the sediment occupying several times the volume of the charcoal.

Due to the high precipitating power of the technical Norite, it was decided to use 0.1 gram portions. These weighed portions were placed in 250 cc. Non-Sol bottles. Portions of iron oxide sol amounting to 100 cc. were added and rotated for the given period of time. Finally the centrifuged sol was analyzed for total iron content in the manner already described. Three sols of widely differing "purity" were used. The results are given in Tables VIII, IX and X, and in Figure 2.

TABLE VIII

PRECIPITATION OF IRON OXIDE SOL NO. 2 BY TECHNICAL NORITE

0.1 gram Technical Norite. 100 cc. portions of diluted sol No. 2. Equivalent Fe/Cl = 19.3 Exposure 4 days

Concentration of the Diluted Sols (C_1) Fe ₂ O ₃ /100 cc. mgs.	Concentration of the Treated Sol (C_2) Fe ₂ O ₃ /100 cc. mgs.	Fe ₂ O ₃ Precipitated (C_1) - (C_2) mgs.
24.3	0.0 *	24.3
41.9	0.0 *	41.9
49.5	0.0 *	49.5
74.2	6.1	68.1
80.5	54.3	25.1
85.5	85.7	— 0.2
93.4	93.8	— 0.4
135.6	136.7	— 1.1
226.3	228.7	— 2.4
389.3	391.5	— 2.2

* Supernatant liquid gave a negative test for ferric ion, when treated with hydrochloric acid and ammonium thiocyanate.

TABLE IX

PRECIPITATION OF IRON OXIDE SOL NO. 4 BY TECHNICAL NORITE

0.1 gram Technical Norite, 100 cc. portions of diluted sol No. 4.
Equivalent Fe/Cl = 25.6. Exposure 4 days.

Concentration of the Diluted Sols (C_1) $\text{Fe}_2\text{O}_3/100$ cc. mgs.	Concentration of the Treated Sol (C_2) $\text{Fe}_2\text{O}_3/100$ cc. mgs.	Fe_2O_3 Precipitated (C_1) - (C_2) mgs.
37.5	0.0	37.5
85.9	0.0	85.9
100.5	0.0	100.5
105.4	0.0	105.4
110.0	0.0	110.0
115.9	5.9	110.0
119.2	11.5	107.7
123.2	38.3	84.9
126.4	69.8	56.6
129.5	72.5	57.0
134.7	101.4	33.3
140.6	128.2	12.4
203.7	205.0	-1.3
267.1	269.0	-1.9

TABLE X

PRECIPITATION OF FERRIC OXIDE SOL NO. 6 BY TECHNICAL NORITE

0.1 gram Technical Norite, 100 cc. portions of the diluted sol No. 6
Equivalent Fe/Cl = 30.9. Exposure 80 hours.

Concentration of the Diluted Sols (C_1) $\text{Fe}_2\text{O}_3/100$ cc. mgs.	Concentration of the Treated Sol (C_2) $\text{Fe}_2\text{O}_3/100$ cc. mgs.	Fe_2O_3 Precipitated (C_1) - (C_2) mgs.
111.0	0.0	111.0
122.1	0.0	122.1
140.2	0.0	140.2
148.9	4.7	144.2
154.1	7.3	146.8
159.9	35.6	124.3
174.9	91.8	83.1
179.4	111.7	67.7
194.8	174.5	20.3
221.9	219.6	2.3
284.1	285.9	-1.8
312.6	314.6	-2.0

The data in the three foregoing tables show three distinct effects:

1. With the weaker sols, there is complete flocculation, with a clear water white supernatant liquid.
2. The mid-figures show incomplete precipitation. In this region, the completeness of precipitation decreases as the concentration of the sol increases. The centrifuged sol is turbid and may more properly be called a fine suspension.
3. At higher concentrations, there is no precipitation. To all out-

ward appearances the sol has suffered no change. It is clear, transparent and of the same approximate color.

ACTION OF TECHNICAL NORITE ON FERRIC OXIDE SOLS.

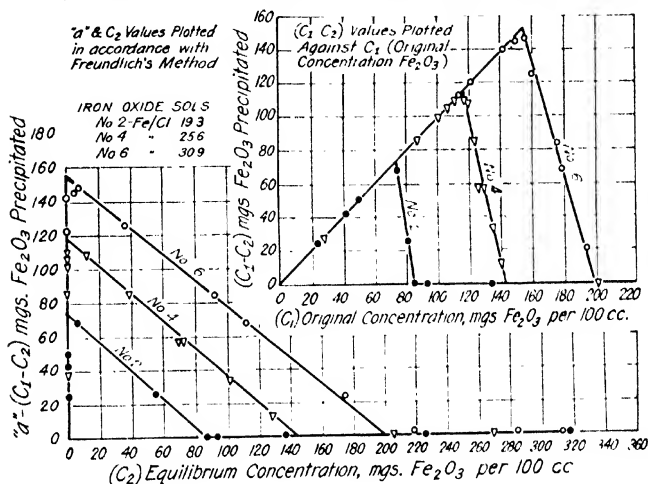


FIG. 2

In accordance with customary adsorption curves, the data have been plotted with the " Fe_2O_3 precipitated" on the vertical, and the equilibrium concentration of ferric oxide on the horizontal. Curves are also given in which the original concentration of ferric oxide is expressed on the horizontal axis (Figure 2).

Action of Blood Charcoal on Iron Oxide Sols:

With these at first wholly unexpected results at hand for technical Norite, it was decided to make similar tests with a charcoal of animal origin. At first, bone charcoal was tested qualitatively for its precipitating power on iron oxide sol. This was found to be so great as to be unfeasible from the viewpoint of the analytical procedure. Small quantities of the charcoal would require very high concentration of sol in order to avoid complete precipitation.

Blood charcoal was tried, and it also was found to have high precipitating power, but less than that of the bone charcoal. Hence it was decided to use blood charcoal in a series of quantitative tests. For the purpose of limiting the requirements of supply of iron oxide sols, 0.05 gram portions of the charcoal were treated with 50 cc. por-

tions of the sols. The results of these tests are given in the Tables XI, XII and XIII, and in Figure 3.

TABLE XI

PRECIPITATION OF IRON OXIDE SOL NO. 2 BY BLOOD CHARCOAL

0.05 gram Blood Charcoal. 50 cc. of the diluted sol. Equivalent Fe/Cl = 19.3.
Exposure 50 hours.

Concentration of the Diluted Original Sols (C_1) Fe ₂ O ₃ /100 cc. mgs.	Concentration of the Treated Sol (C_2) Fe ₂ O ₃ /100 cc. mgs.	Fe ₂ O ₃ Precipitated (C_1)—(C_2) mgs.
209.3	0.0	209.3
274.3	0.0	274.3
315.8	27.4	288.4
340.5	153.7	186.8
345.6	313.7	31.9
373.0	370.5	2.5
390.6	391.6	— 1.0

TABLE XII

PRECIPITATION OF IRON OXIDE SOL NO. 1 BY BLOOD CHARCOAL

0.050 gram Blood Charcoal. 50 cc. of the diluted sol. Equivalent Fe/Cl = 17.9.
Exposure 48 hours.

Concentration of the Diluted Original Sols (C_1) Fe ₂ O ₃ /100 cc. mgs.	Concentration of the Treated Sol (C_2) Fe ₂ O ₃ /100 cc. mgs.	Fe ₂ O ₃ Precipitated (C_1)—(C_2) mgs.
205.0	0.0	205.0
212.1	9.4	202.7
214.0	10.3	203.7
218.7	61.2	157.5
231.6	69.0	162.6
240.2	183.2	57.0
247.1	207.7	39.4
253.4	251.2	2.2
305.3	304.3	1.0
362.7	361.8	0.9
602.3	605.5	— 3.2

TABLE XIII

PRECIPITATION OF IRON OXIDE SOL NO. 6 BY BLOOD CHARCOAL

0.05 gram Blood Charcoal. 50 cc. diluted sol. Equivalent Fe/Cl = 30.9.
Exposure 50 hours.

Concentration of the Diluted Original Sols (C_1) Fe ₂ O ₃ /100 cc. mgs.	Concentration of the Treated Sol (C_2) Fe ₂ O ₃ /100 cc. mgs.	Fe ₂ O ₃ Precipitated (C_1)—(C_2) mgs.
479.2	0.0	479.2
527.1	0.0	527.1
551.1	0.0	551.1
599.2	5.9	593.3
707.7	230.6	477.1
765.8	514.9	250.9
788.6	540.2	248.4
842.3	801.4	40.9

ACTION OF BLOOD CHARCOAL ON IRON OXIDE SOLS.

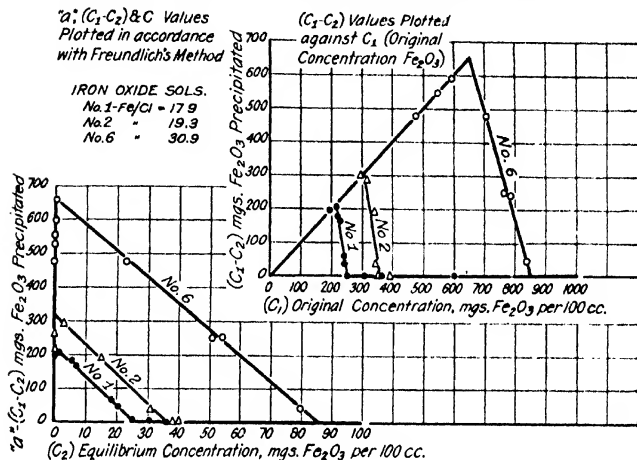


FIG. 3.

Precipitation Across a Membrane:

Another experiment should be described here, in support of a proposed explanation for this type of curve, to be stated immediately hereafter.

A portion of technical Norite amounting to one gram was placed in a small collodion bag, attached by stopper to a funnel, and water added through the funnel. The bag was immersed about two-thirds of its depth in an iron oxide sol, contained in a bottle and protected from the air by another stopper, through which the stem of the funnel passed. By the next morning, sufficient soluble impurities had diffused through the walls of the bag to produce a complete precipitation of the iron oxide sol, leaving a clear water white supernatant liquid.

This test was repeated, using blood charcoal with the same result,—the precipitate in this case being less gelatinous and more flocculent,—the sol was completely precipitated.

The same test was repeated using purified animal charcoal, purified Norite and sugar charcoal, continuing the exposure at least three days in each case, and in the case of these three charcoals, there was no sediment or precipitation, and apparently there had been no change whatever in the sol.

Explanation of the Precipitating Action of Technical Grade Charcoals on Iron Oxide Sol:

The explanation offered for this type of curve is the one that seems obvious at first thought, and in fact possibly the only one that can fit the facts in the case.

Purified charcoals are found to have no precipitating effect on iron oxide sols, while technical grade charcoals containing soluble mineral substances are found to have quite characteristic precipitating action, even through a collodion membrane.

Considering any one of the curves, e.g., Figure 2; Action of 0.1 gram portions of technical Norite on sol #6: In this quantity of the technical Norite, there is a given quantity of soluble electrolyte which diffuses out into the sol. This quantity of electrolyte exceeds the liminal value of the sols of the dilutions up to 0.154 gram iron oxide per 100 cc.⁴ and there is complete precipitation. With a sol of very slightly higher concentration of iron, e.g., 0.160 gram iron oxide per 100 cc., there is present a slight excess of iron oxide with its stabilizing electrolyte, sufficient to hold the iron oxide up in the state of a muddy suspension, but not enough to keep the whole mass in a true transparent colloidal state. It is believed that this is the state throughout the sharply dropping region of the curve. When the sol contains as much as 0.20 gram iron oxide per 100 cc., no precipitation occurs. The sol remains transparent, and to all outward appearances, is unchanged. It is believed, however, that the condition of the sol at this point of the curve is that state of highest "purity," i.e., greatest Fe/Cl ratio, at which the sol can remain clear and stable.

The explanation proposed for the precipitating action of blood charcoal on iron oxide sol is the same as the foregoing.

The fact that when the maxima points of the precipitation curves (Figures 2 and 3) are plotted against the "purity" of the respective sols straight line curves are obtained (Figure 4), is another indication that the functioning of the liminal value principle is responsible for the characteristic features of these precipitation curves. It is known that the "purer" the sol, the more easily it is precipitated by electrolytes. Thomas and Frieden⁵ believe that the stability of ferric oxide sol, stabilized by ferric chloride, is due to the solubility (solution forces) of the adsorbed ferric chloride in the dispersion medium. Hence the "purer" the sol, the more easily electrolytes should precipitate it and the lower its liminal value should be. Quite in harmony with this indication is the finding of Weiser and Nicholas⁶ that for an iron oxide sol of given purity the "Ratio of Precipitating Values" (i.e., Ratio of

⁴ The total iron content is expressed as Fe_2O_3 for convenience, and as an approximation of the true state of the iron.

⁵ Thomas and Frieden, *J. Am. Chem. Soc.*, **45**, 2522-32 (1923).

⁶ Weiser and Nicholas, *J. Phys. Chem.*, **25**, 743 (1921).

concentrations of electrolytes necessary to give complete precipitation) when plotted against concentrations of various dilutions of the sol, gave a straight line curve almost at forty-five degrees, particularly

RELATIONSHIP OF MAXIMUM POINTS OF IRON OXIDE
PRECIPITATION CURVES

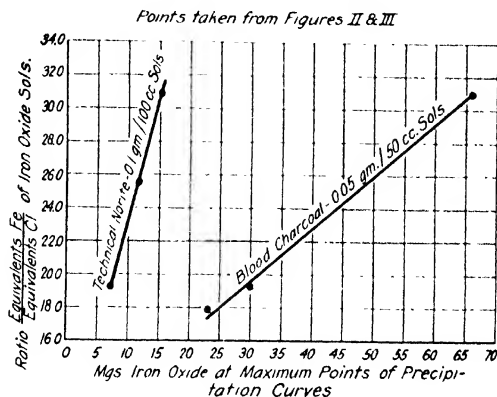


FIG. 4.

for high valence precipitating ions, which makes the liminal value of an iron oxide sol of given purity approximately directly proportional to its concentration, the more concentrated the sol, the greater the liminal value.

Action of Charcoals on Ferric Chloride Solutions.

In order to obtain information concerning the component of the iron oxide sol involved in these precipitations by technical charcoals, tests were made with all five charcoals previously named, on ferric chloride solutions. The charcoal samples were treated with the freshly prepared ferric chloride solutions, because at the concentrations used, within several days, hydrolysis materially altered the appearance and transparency of the solutions.

One gram portions of charcoal, in Non-Sol glass stoppered bottles were treated with 100 cc. portions of a series of diluted ferric chloride solutions for four days. During this period the samples were rotated at least 12 hours, and shaken by hand at intervals during the remainder of the period of the test. They were finally centrifuged, and 50 cc. aliquots were withdrawn for analysis in the same manner as already

stated for analysis of iron oxide sols. The total iron content was calculated to FeCl_3 .

The results for purified Norite, purified bone charcoal, and sugar charcoal are given in Table XIV; for technical Norite in Table XV and Figure 5; and for blood charcoal in Table XVI and Figure 7.

TABLE XIV
SORPTION OF FERRIC CHLORIDE BY VARIOUS CHARCOALS

1 gram charcoal 100 cc. FeCl_3 solution. Exposure 4 days.			
Stock Solution FeCl_3 per 100 cc. mgs.	Purified Norite FeCl_3 Sorbed mgs. *	Purified Bone Charcoal FeCl_3 Sorbed mgs. *	Sugar Charcoal FeCl_3 Sorbed mgs. *
54.0	3.8	0.9	1.1
59.6	2.2	0.2	1.4
66.8	2.8	0.5	1.2
78.4	2.5	0.1	2.4
85.5	3.0	0.4	0.4
118.8	2.6	1.3	1.3
240.6	5.3	3.3	2.3
345.5	4.9	3.3	5.0

* Difference between original and equilibrium concentration of iron expressed as FeCl_3 .

Note: The centrifuging removed the Sugar charcoal and the purified animal charcoal perfectly, but was not quite so effective in the case of the purified Norite.

During the time-interval of these tests, the stock solutions from which the 100 cc. test portions had been withdrawn, became quite turbid, while the centrifuged charcoal-treated solutions were perfectly transparent, the degree of color decreasing toward the higher concentrations.

The foregoing table shows the absence of any appreciable sorption of ferric chloride by purified charcoals.

In the cases of technical grade charcoals, positive removal was obtained, as shown by Tables XV and XVI and Figures 5 and 7.

It was noted that the supernatant liquid in the reaction bottles 6 to 13 (Table XV) graded in color from yellowish brown to reddish brown. These colors were appreciably darker than those of the original stock solutions of ferric chloride used in the tests. As long as the reaction bottles were unopened the graded range of color was not perfectly apparent to the eye, but about one week after the bottles had been opened for withdrawal of sample for analysis, the graded colors had developed quite characteristically.

To determine whether the brown color was due to the presence of ferric oxide sol, about 15 cc. of the contents of test bottle #10 (Table

TABLE XV
ACTION OF TECHNICAL NORITE UPON FERRIC CHLORIDE

1 gram technical Norite. 100 cc. of the diluted FeCl_3 solution. Rotated 24 hours.
Exposure 5 days.

No.	$\text{FeCl}_3/100$ cc. in Original Stock Solution (C_1) mgs.	$\text{FeCl}_3/100$ cc. in Treated Solutions (C_2) mgs.	FeCl_3 Precipitated ($C_1 - C_2$) mgs.
1	54.0	0.0 *	54.0
2	57.1	0.0 *	57.1
3	59.6	0.0 *	59.6
4	59.9	0.0 *	59.9
5	64.8	5.6	59.2
6	66.8	37.3	29.5
7	73.6	57.5	16.1
8	78.4	64.4	14.0
9	85.5	74.3	11.2
10	118.8	110.2	8.6
11	240.6	232.0	8.6
12	329.0	320.1	8.9
13	345.5	334.0	11.5

* Tests for ferric ion with ammonium thiocyanate were negative

ACTION OF TECHNICAL NORITE ON FERRIC CHLORIDE SOLUTION

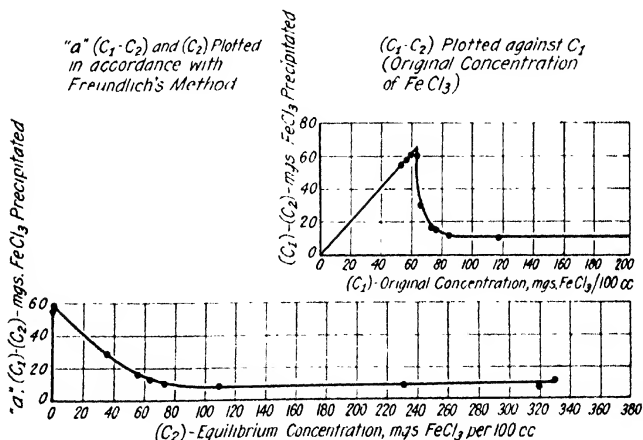


FIG. 5.

XV) was filtered through ordinary filter paper into a test tube shaped collodion sack and dialyzed against 200 cc. of distilled water for 24 hours. At the end of this period of time the contents of the sack had

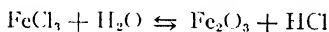
gained in transparency and gave every appearance of a dilute reddish brown ferric oxide sol. The diffusate was colorless and showed but an exceedingly faint test for ferric ion.

The content of the sack was divided into two equal portions. To one portion, a pinch of sodium chloride crystals was added, and both liquids centrifuged after a few minutes. The half that had received the sodium chloride gave a water white supernatant liquid and a separated solid while the other half had not been altered in appearance.

This proves that the sack contained ferric oxide hydrosol. This transformation of ferric chloride to ferric oxide sol seems to be most pronounced in that region of the curve corresponding to the rapidly falling portion.

That this is to be expected when ferric chloride is treated with any alkaline charcoal, i.e., practically all vegetable charcoals, may be seen from the following consideration.

Ferric chloride in aqueous solution is always in hydrolytic equilibrium with hydrochloric acid. One way of representing this hydrolysis is:



It is to be noted that the portion of the equation underscored represents iron oxide sol, which is frequently expressed as $x \text{ Fe}_2\text{O}_3$, $y \text{ FeCl}_3$, $z \text{ H}_2\text{O}$.

Upon treating ferric chloride solutions with technical Norite, the alkali of the latter, at the lower dilutions of the ascending portion of the curve (Figure 5), neutralizes all the hydrolytic hydrochloric acid producing complete precipitation. At the higher concentrations of the ascending portion of the curve, the alkali neutralizes sufficient of the hydrochloric acid to produce iron oxide sol, which, however, does not persist, due to the precipitating or salting out effect of the electrolytes present. For the descending portion of the curve, the ferric oxide sol there formed possesses sufficient stabilizing ferric chloride to withstand the precipitating effect of electrolytes present. The solutions represented by the horizontal portion of the curve may be considered as ferric chloride solutions of decreasing degrees of hydrolysis, or as ferric oxide sols of decreasing degrees of purity.

When ferric chloride is precipitated by an alkali, the hydrous iron oxide cannot remain undissolved in the presence of excess ferric chloride solution. Thomas Graham⁷ proposed a method of preparing iron oxide sol by agitating hydrous ferric oxide with ferric chloride solutions.

One might question whether this can occur in the presence of charcoal. To answer this question, the following experiment was made: 0.20 gram technical Norite was treated with 100 cc. of diluted sol #8,

⁷ *Proc. Roy. Soc. London*, 13, 335 (1863-4).

containing 0.1352 gram Fe. The reaction was complete within two hours, giving complete flocculation of the sol, and upon settling, a perfectly clear water white supernatant liquid. Five drops of a 2.7 molar ferric chloride solution were added, and the whole shaken and then let stand. By next morning, the supernatant liquid was a deep reddish brown iron oxide sol.

In such experiments it is within the possibilities that the reaction of the alkali of the charcoal with the hydrolytic hydrochloric acid in conjunction with the precipitating action of other electrolytes of the charcoal, might leave slight quantities of iron oxide on the surface or within the interstices of the charcoal, which would remain there until

ACTION OF TECHNICAL NORITE ON FERRIC CHLORIDE SOLUTIONS - PLOTTED AGAINST TIME

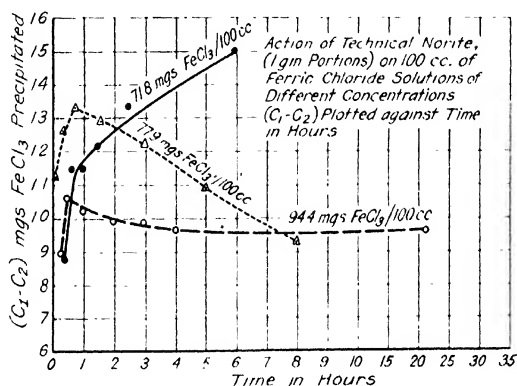


FIG. 6.

the reverse peptizing process could take it back into solution as iron oxide sol., i.e., that there might be a lag in the curve that could be demonstrated experimentally. An attempt was made to demonstrate such a lag in the re-solution of any such momentarily precipitated ferric oxide.

A quantity of ferric chloride solution with a concentration corresponding to the lower region of the dropping part of the curve in Figure 5 was prepared. Portions of this solution amounting to 100 cc. were added to 1 gram samples of technical Norite in glass stoppered Non-Sol bottles. After the specified time of exposure with continual rotation, the contents were centrifuged 10 minutes and an aliquot analyzed for total iron content expressed as ferric chloride.

This was repeated with two other concentrations of ferric chloride solutions (Figure 6).

The curves plotted in Figure 6 are interpreted as demonstrating a lag between the tendency of the alkali carbonate of the charcoal to precipitate the ferric chloride as Fe_2O_3 and the tendency of the ferric chloride solution to redissolve any precipitated Fe_2O_3 as iron oxide sol. The lower the iron chloride concentration, the greater the lag. The upward trend of the curves represents the predominating influence of the original relatively high alkali carbonate concentration and at the same time the fact that its diffusion out of the charcoal requires a definite period of time. Theoretically the curve should have the approximate form of a pyramid.

Action of Blood Charcoal on Ferric Chloride Solutions.

TABLE XVI

PRECIPITATION OF FERRIC CHLORIDE BY BLOOD CHARCOAL

1 gram Blood charcoal. 100 cc. of the diluted FeCl_3 solution.
Exposure 6 days.

No.	$\text{FeCl}_3/100$ cc. in Original Stock Solution C_1 mgs.	$\text{FeCl}_3/100$ c.c in Treated Solutions C_2 mgs.	FeCl_3 Precipitated $C_1 - C_2$ mgs.
1	54.0	0.0 *	54.0
2	59.6	0.0 *	59.6
3	66.8	0.0 *	66.8
4	78.4	0.0 *	78.4
5	85.5	0.0 *	85.5
6	118.8	0.0 *	118.8
7	240.6	24.4	216.2
8	318.1	93.7	224.4
9	338.1	114.5	223.6
10	363.2	135.6	227.6
11	384.5	155.1	229.4
12	426.0	195.4	230.6
13	557.7	334.0	223.7

* Gave no test for ferric ion with hydrochloric acid and ammonium thiocyanate.

The following notes were recorded during this series of tests:

(1) The charcoal in the test bottles settle out quite clearly by gravity. However, before analyzing the supernatant liquid, it was centrifuged for the sake of uniformity of procedure. The centrifuged solutions were beautifully clear and transparent grading in depth of color toward #13 (Table XVI), which was deepest yellow. The yellow is that of ferric chloride. There is clearly no iron oxide sol formation.

(2) The sediment in the bottles after settling out by gravity occupied a much enlarged volume over that of the charcoal. It appeared to be charcoal interspersed or coated over with some brownish dirt colored iron compound.

(3) The clear supernatant ferric chloride solution, after being made alkaline with ammonia, and filtered, gave a positive test for calcium showing that calcium had come out of the charcoal.

(4) When, in the analysis of the treated solution, the aliquot was evaporated to white fumes with 3.8 molar sulfuric acid, a considerable amount of gelatinous meta silicic acid became apparent. It was necessary to continue the evaporation to perfect dryness and then to dry heat for one half hour, before taking up with dilute sulfuric acid. This step was necessary in order to prevent subsequent clogging and poor filtration through the Jones Reductor.

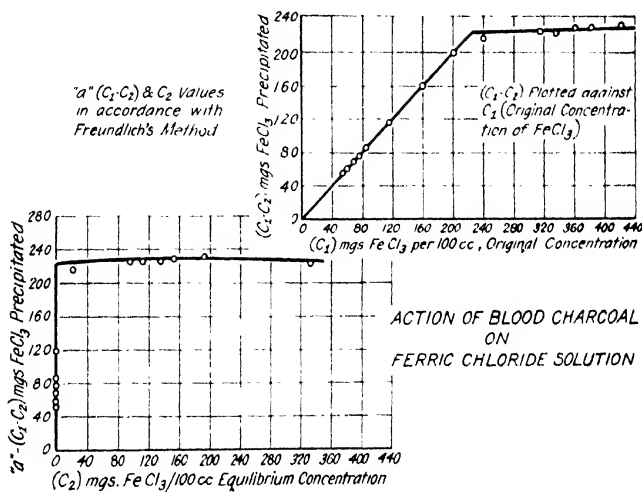


FIG. 7.

The character of the curves for blood charcoal differ from those of technical Norite in that the precipitation reaches a maximum value and then remains constant for the higher concentrations of ferric chloride. The supernatant liquids were a beautiful clear light lemon yellow, showing no apparent tendency toward the formation of iron oxide sol. The fact that calcium and metasilicic acid appear in appreciable quantity in the solution for analysis is believed to give the clue for the explanation of this difference in the curves.

The mechanism of the predominating reaction in the action of blood charcoal on ferric chloride solution is considered to be as follows: Hydrolytic hydrochloric acid from the ferric chloride reacts with some easily transposable silicate of calcium in the charcoal liberating silicic

acid and calcium chloride, the iron precipitating as iron oxide or some basic iron silicate.

This explanation is in harmony with the fact that in the action of blood charcoal on iron oxide sol (Figure 3), a reversal of the precipitation occurs, so that in the outer regions of the curves, the precipitation falls to zero. The iron oxide sol was of course free of all acidity other than that minute amount which is invariably present in hydrolytic equilibrium with the dispersed phase. F. L. Browne⁸ has shown that the activity of hydrogen ion falls very rapidly with increasingly higher purities of the sol. Thomas and Frieden⁵ found that their pure iron oxide hydrosols had a hydrogen ion concentration of 10^{-5} . Due to this absence of appreciable acidity, silicic acid was not liberated from the charcoal, so that the normal effect of excess of ferric oxide sol, with its excess of stabilizing electrolyte over and above that requisite for stability, operated to reverse any precipitating action of the, in the main, water soluble electrolytes of the charcoal, at those concentrations where the liminal value of the sol was not exceeded.

From Table XVI and Figure 7 it is seen that 1 gram of blood charcoal precipitates 0.224 gram FeCl_3 from 100 cc., which is equivalent to 0.0138 moles ferric chloride per liter and if the hydrolytic hydrochloric acid or its equivalent acidity were left entirely behind in the solution its concentration would be 0.0414 moles per liter. It is believed that ferric oxide sol could not exist in the presence of such a concentration of hydrogen ion.

Action of Purified and Technical Norite on Hydrochloric Acid Solutions.

In view of the fact that purified charcoals were found to be devoid of any appreciable adsorbing powers on both iron oxide sol and ferric chloride solution, and also of the fact that interaction of hydrochloric acid enters into the explanation offered for the precipitating action of technical grade charcoals on ferric chloride solution in particular, it was considered desirable to make some tests demonstrating the removal of hydrochloric acid by a purified and technical grade charcoal.

A series of very dilute hydrochloric acid solutions, of a strength equivalent to the ferric chloride test solutions described in Table XV were prepared. These were standardized with carbon dioxide-free sodium hydroxide, using phenolphthalein indicator.

Technical and purified Norite, in one gram portions, were treated with 100 cc. of each of these standardized acid solutions. After three days, during which the test bottles were frequently agitated, an aliquot of the clear supernatant liquid was titrated for acidity as in the case of the standardizations of the original solutions.

⁸ *J. Am. Chem. Soc.*, **45**, 297-311 (1923).

ADSORPTION OF FERRIC OXIDE HYDROSOL 351

In the case of the technical Norite, aliquots were also analyzed gravimetrically for chloride ion.

The results of these tests are given in Tables XVII and XVIII and in Figure 8.

TABLE XVII
SORPTION OF HYDROCHLORIC ACID BY PURIFIED NORITE

1 gram purified Norite, 100 cc hydrochloric acid solution.
Exposure 3 days.

HCl in Original Solution * (C ₁) moles/100 cc.	HCl in Solution at Equilibrium * (C ₂) moles/100 cc.	"A" HCl "Adsorbed" moles
0.000233	0.000123	0.000110
0.000521	0.000370	0.000151
0.000784	0.000627	0.000157
0.000869	0.000693	0.000176
0.001105	0.000932	0.000173
0.001687	0.001490	0.000197
0.002056	0.001852	0.000204
0.002997	0.002792	0.000205
0.003759	0.003530	0.000229
0.005254	0.005003	0.000251

* By titration with carbon dioxide free sodium hydroxide

TABLE XVIII
REMOVAL OF HYDROGEN ION AND CHLORIDE ION FROM HYDROCHLORIC ACID
SOLUTION BY TECHNICAL NORITE

Test No.	HCl in Original Solution * (C ₁) moles/100 cc.	Hydrogen Ion in Solution at Equilibrium * (C ₂) moles/100 cc	Hydrogen Ion Removed "A" moles	Chloride Ion in Solution at Equilibrium † (C ₂) moles/100 cc.	Chloride Ion Removed "A" moles
1	0.000233	0.0000 ‡	0.000233	0.000252	— 0.000019
2	0.000521	0.000016	0.000505	0.000504	0.000017
3	0.000784	0.000038	0.000746	0.000724	0.000060
4	0.000869	0.000049	0.000820	0.000816	0.000053
5	0.001105	0.000074	0.001031	0.000980	0.000125
6	0.001687	0.000518	0.001169	0.001452	0.000235
7	0.002056	0.000864	0.001192	0.001796	0.000260
8	0.002997	0.001760	0.001237	0.002684	0.000313
9	0.003759	0.002511 §	0.001248	0.003448	0.000311
10	0.005254	0.003965 §	0.001289	0.004940	0.000314

* By titration with carbon dioxide free sodium hydroxide solution, using phenolphthalein indicator.

† By precipitation as AgCl in presence of nitric acid

‡ Alkaline to phenolphthalein

§ Neutral solution gave a test for calcium.

In the case of the technical Norite, the neutralized solution in tests 9 and 10, Table XVIII, were found to give a quite appreciable test for calcium. Also the fact that the endpoint of the titration of the test

solutions was not nearly as sharp and decisive as in the case of the original hydrochloric acid stock solutions indicates the probability of the presence of a "weak" acid, possibly silicic or phosphoric.

These tests show that purified Norite adsorbs hydrochloric acid to a slight extent, while technical Norite removes it to a much greater extent, the removal being due to (1) the same cause operating as for the purified charcoal, and (2) "exchange adsorption" involving a metathetical reaction between the hydrochloric acid and some compound of calcium in the charcoal, this reaction accounting for fully 75 per cent of the removal within the range of concentration 0.0 to 0.004 molar acid (Figure 8).

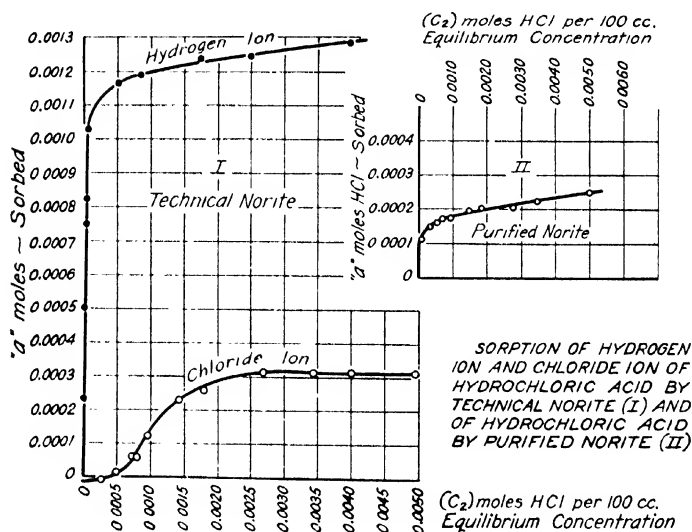


FIG. 8

It is seen that the "total acidity" method does not represent the true removal of hydrochloric acid, since the chloride ion as determined gravimetrically is removed to a much less extent than the hydrogen ion. The fact that technical Norite contains water soluble chlorides makes it probable that the true removal of chloride ion is appreciably more than that represented in the Tables XVII and XVIII and Figure 8.

The data upon which the removal of hydrochloric acid by purified Norite is based was obtained by titrations of total acidity using phenolphthalein. Since, in the case of technical Norite, this method is found to give results that are not equivalent to the chloride ion sorption as

determined gravimetrically, it might be questioned to what extent acidimetric methods represent the true adsorption of hydrochloric acid by purified Norite.

Summary.

The following listed facts have been shown to be true, or have been indicated to be true:

1. Purified charcoals have been found to have no adsorbing action on iron oxide sols of the type known as Graham iron oxide sols.
2. Technical grade charcoals have high removal powers on iron oxide sols and in this removal any adsorption effect is wholly negligible, the removal being due to the precipitating action of the electrolytes present in the charcoal as impurities.
3. Technical grade charcoals containing soluble mineral impurities have high precipitating power on iron oxide sols, the principle of the "Liminal Value" operating to cause the curves for such precipitations to take the characteristic form as shown in Figures 2 and 3. It is believed that this type of curve is a general one for the action of charcoals on intermediate and hydrophobic sols.
4. By plotting the maxima of the precipitation curves for different iron oxide sols against the "purities" of the sols used (Figure 4), straight line curves are obtained, showing that the liminal value is a straight line function of the purity, in the case of iron oxide sols.
5. Purified charcoals have almost negligible if any adsorbing power on ferric chloride solutions at least at concentrations up to 0.02 molar. Technical grade charcoals exert a precipitating action on ferric chloride solutions, alkaline and acid charcoals giving different types of curves. An explanation based on "Exchange Adsorption" with supporting evidence, is given for the precipitation effects in each case.
6. Purified and technical grade Norite exert removal powers toward hydrochloric acid, that of the purified Norite being slight while that of the technical Norite is high. Removal curves determined by "acidimetric" (titration with alkali) and gravimetric (weighing chloride as AgCl) methods are quite different, and show that up to 0.004 molar hydrochloric acid only about one-fourth as many moles of chloride ion are removed as of hydrogen ion. This is further support for the explanations mentioned in item 5 above.
7. Sufficiently purified charcoal has no precipitating action on gold sols. With less pure charcoals, precipitation occurs and the principle of the liminal value is probably followed.

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IONIC ANTAGONISM IN COLLOID SYSTEMS

By HARRY B. WEISER

I. Ionic Antagonism in the Neutralization of Sols by Single Electrolytes.

In the precipitation by electrolytes of sols stabilized by preferential adsorption of ions, it is usually considered that only anions count in the case of positive sols and only cations count in the case of negative sols. However, it was recognized by Freundlich¹ a score of years ago that the critical precipitation concentration of electrolytes for sols may be influenced by the ion having the same charge as the sol; and a decade ago Bancroft² pointed out that the amount of electrolyte required to precipitate any given suspension will vary with the nature of the cation, the anion, and the disperse phase. This point of view does not seem to have been taken seriously by many people; but in 1920, attention was called³ to the fact that the influence of the ions having the same charge as the sol cannot be disregarded entirely in any case, and may be quite marked if the electrolyte precipitates only in high concentration. The precipitation value of electrolytes for sols may be defined, therefore, as that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion added with the precipitating solution. There is thus an antagonistic action between the oppositely charged ions of a precipitating electrolyte in the sense that the greater the adsorption of the stabilizing ion the greater must be the adsorption of the precipitating ion to effect neutralization. Hence the precipitation value of an electrolyte with a strongly adsorbed stabilizing ion is necessarily higher than that of an electrolyte with a weakly adsorbed stabilizing ion. This is illustrated in Table I which gives the precipitation values in milliequivalents per liter of potassium salts for different arsenious sulfide sols. The order of precipitating power of the potassium salts is: chloride > sulfate > ferrocyanide > citrate, which is probably the order of increasing adsorbability of the stabilizing anions.

Just as the precipitating power of an electrolyte decreases with increasing adsorbability of the antagonistic stabilizing ion so the precipi-

¹ "Kapillarchemie," 352 (1909); *Z. physik. Chem.*, **44**, 104 (1903).

² *J. Phys. Chem.*, **19**, 368 (1915).

³ Weiser, *J. Phys. Chem.*, **24**, 30 (1920).

TABLE I

Concentration of Sol Grams per Liter		18	3.7	60
Precipitation value of	KCl	49.5	85	33.2
	K ₂ SO ₄	65.5	100	43.5
	K ₄ Fe(CN) ₆	—	185	71.2
	K ₂ Cit	240	270	—
Investigator		Freundlich ^a	Ghosh and Dhar ^b	Weiser and Nicholas ^c

tating power of electrolytes with the same stabilizing ion increases with increasing adsorbability of the precipitating ion. This is illustrated in Table II⁷ which gives the precipitation value of barium chloride and of various alkali chlorides for arsenious sulfide together with the adsorption of barium during the precipitation of the sol with barium chloride alone and when mixed with constant amount of the several alkali chlorides. From the observations it will be noted that univalent ions cut down the adsorption of barium in the order, lithium < sodium < potassium < hydrogen. Since, under otherwise constant conditions, one should expect the adsorption of a given cation to be cut down by the presence of a second cation in proportion to the adsorbability of the latter, it follows that the order of adsorbability of the univalent ions is: hydrogen > potassium > sodium > lithium. This is exactly the same as the order deduced from the precipitation values of the salts assuming that the salt containing the most readily adsorbed cation precipitates in lowest concentration.

TABLE II

Electrolyte Added to 100 cc Sol Total Volume 200 cc	Barium Adsorbed		Precipitation Value Millicq. per Liter
	Grams	Millicq. per Gram	
30 cc. N/50 BaCl ₂	0.0109	0.058	BaCl ₂ 2.74
30 cc. N/50 BaCl ₂ + 30 cc. N/2 LiCl	0.0037	0.019	LiCl 88.7
30 cc. N/50 BaCl ₂ + 30 cc. N/2 NaCl	0.0025	0.014	NaCl 73.5
30 cc. N/50 BaCl ₂ + 30 cc. N/2 KCl	0.0018	0.009	KCl 63.7
30 cc. N/50 BaCl ₂ + 30 cc. N/2 HCl	0.0013	0.007	HCl 52.5

It should be pointed out in passing that the results recorded in Table II furnish almost conclusive proof that the univalent cations are adsorbed less strongly than bivalent barium. For example the adsorption of barium is cut down but very little by the presence of an equivalent amount of lithium, and 25 times the concentration of lithium cuts it down but two-thirds of the value in the absence of lithium.

^a *Z. physik. Chem.*, **44**, 129 (1903)

^b *Kolloid-Z.*, **36**, 129 (1925)

^c *J. Phys. Chem.*, **25**, 742 (1921).

^d Weiser, *J. Phys. Chem.*, **25**, 955 (1921).

II. Ionic Antagonism in the Neutralization of Sols by Mixtures.

Thirty years ago Linder and Picton⁸ observed that the precipitating action of mixtures of two electrolytes for arsenious sulfide sol, is approximately additive provided the precipitating power of each is of the same order of magnitude, whereas the precipitating action may rise appreciably above an additive relationship if the electrolytes vary widely in their precipitating power. Thus the precipitating action of mixtures of SrCl_2 and BaCl_2 are nearly additive, whereas the addition of potassium chloride increases rather than decreases the precipitation concentration of strontium chloride. This cannot be attributed to a decrease in the dissociation of strontium chloride by potassium chloride because other potassium salts, such as the nitrate, give similar results.

As a result of an investigation of this anomalous behavior in 1921,⁹ it was concluded that, in the simultaneous adsorption by solids from mixtures of two electrolytes having no ion in common, the most readily adsorbed cation and anion are taken up most and the other pair least readily; while from mixtures having one ion in common, the oppositely charged ions are each adsorbed less than if the other were absent but the most readily adsorbed ion is displaced the least. From this, there would appear to be two factors which influence the precipitating action of mixtures of electrolytes: (1) The antagonistic effect of each precipitating ion on the adsorption of the other and (2) the stabilizing influence of the ions having the same charge as the sol.

TABLE III
PRECIPITATION OF COLLOIDAL As_2S_3 WITH MIXTURES OF LiCl AND BaCl_2

N/2 LiCl Taken cc.	Taken cc.	N/100 BaCl_2 to Complete Calculated cc.	Coagulation cc.	Difference Per Cent
4.05	4.03			
0.5	4.50	3.54	0.96	27
1.0	4.25	3.03	1.22	38
2.0	3.76	2.03	1.73	84
3.0	2.25	1.03	1.22	118

As an illustration of the antagonistic action of salts of varying precipitating power the observations with mixtures of LiCl and BaCl_2 on arsenious sulfide sol are given in Table III.¹⁰ It will be seen that the presence of alkali chloride increases appreciably the precipitation concentration of barium chloride. In Table IV is given the effect of the presence of lithium on the adsorption of barium during the precipitation of arsenious sulfide sol. Experiment 1 gives the adsorption of Ba^{++} ion at the precipitation concentration of BaCl_2 ; experiments 2, 3,

⁸ *J. Chem. Soc.*, 67, 67 (1895).

⁹ Weiser, *J. Phys. Chem.*, 25, 665 (1921).

¹⁰ *Ibid.*, 28, 232 (1924).

TABLE IV

ADSORPTION BY ARSENIOS SULFIDE OF BARIUM IN THE PRESENCE OF LITHIUM

Mixtures Added to 125 cc. of Colloid Containing 2.84 g. As_2S_3			BaSO ₄ Remaining in 200 cc.		Barium Adsorbed	
N/2 LiCl	N/100 BaCl ₂	H ₂ O	Average		Gms.	Gms. per Mole As_2S_3
0	50.80	74.20	0.0288	0.0284	0.0140	1.214
0	50.80	74.20	0.0280			
0	56.25	68.75	0.0316	0.0319	0.0151	1.310
0	56.25	68.75	0.0320			
6.25	56.25	62.50	0.0371	0.0373	0.0112	0.971
6.25	56.25	62.50	0.0375			
0	53.10	71.90	0.0304	0.0302	0.0143	1.250
0	53.10	71.90	0.0301			
12.5	53.10	59.40	0.0363	0.0365	0.0097	0.841
12.5	53.10	59.40	0.0368			
0	47.00 *	73.00	0.0259	0.0260	0.0132	1.145
0	47.00	73.00	0.0260			
25.0	47.00 *	48.00	0.0358	0.0357	0.0060	0.520
25.0	47.00	48.00	0.0355			

and 4 give (a) the adsorption Ba^{++} ion from BaCl_2 alone at the concentration necessary to cause precipitation from the mixture with LiCl and (b) the adsorption of Ba^{++} ion in the presence of Li^+ ion. In experiment 4 the concentration of BaCl_2 is below the precipitation value, necessitating the addition of some MgCl_2 . Since the precipitating power of these two salts is very nearly the same, the presence of the small amount of Mg^{++} ion can have little or no effect on the adsorption of Ba^{++} ion at this concentration. Attention should be called to the fact that the concentration of LiCl and BaCl_2 used in experiments 2, 3, and 4 correspond to those of 0.5, 1.0, and 2.0 cc. of LiCl, respectively, in Table III.

From these observations it is obvious that concentrations of lithium below the precipitation value have a marked influence on the adsorption of barium. Thus at the precipitation concentration of a mixture containing one-eighth the precipitation value of LiCl alone the adsorption of Ba^{++} ion is lowered more than 25 per cent; while from a mixture containing one-half the precipitation value of LiCl alone, the adsorption of Ba^{++} ion is decreased 53 per cent. At the same time, the presence of Ba^{++} ion unquestionably influences the adsorption of Li^+ ion so that the concentration necessary for sufficient adsorption to decrease the charge on the particles below the critical value is proportionately greater for each salt in the presence of the other. This mutual ionic antagonism would appear to be an important factor in raising the precipitation concentration of mixtures above the additive value.

Associated with the cationic antagonism is the antagonistic action of chloride, the adsorption of which cannot be ignored at the relatively high concentration of LiCl employed. Until recently, Dhar and his collaborators¹¹ discredited the influence of any cationic antagonism in increasing the precipitation value of certain salt pairs above the additive value, and attributed the effect entirely to the stabilizing action of the anions, chloride ion in the case at hand. Some further observations bear on this point:

In Table II it was pointed out that the same concentration of different alkali chlorides cuts down the adsorption of barium ion to widely different degrees. It seemed probable therefore that the precipitation value of barium chloride would vary in the presence of approximately the same concentration of chloride ion but with different alkali cations. That such is the case is shown clearly by observations recorded in Table V and shown graphically in Figure 1.¹²

TABLE V
PRECIPITATION OF As_2S_3 BY MIXTURES OF $BaCl_2$ AND ALKALI CHLORIDES
(Precipitation values in millieq. per liter.)

LiCl + $BaCl_2$	NaCl + $BaCl_2$	KCl + $BaCl_2$	HCl + $BaCl_2$
0.0	1.60	0.0	1.60
12.5	2.02	1.93	1.88
25.0	2.18	1.98	1.92
43.7	2.13	1.82	1.62
62.5	1.78	1.30	1.05
81.2	1.23	0.00	0.00
111.2	0.00		

It will be noted that the precipitation value of barium chloride is increased by like amounts of alkali chlorides in the order: $LiCl > NaCl > KCl$; while in the presence of HCl, the precipitation value of barium salt first rises to a point just below that in the presence of a like amount of lithium chloride and then drops off rather sharply. Since the adsorbability of the alkalis is in the order: $K > Na > Li$, it may be reasoned that the stabilizing action of chloride ion will be greater in the presence of lithium ion than of potassium ion, thus accounting for the higher precipitation values of barium chloride in the presence of lithium chloride than of potassium chloride. This would not account for the behavior of mixtures of hydrochloric acid and barium chloride for, at certain concentrations of chloride, the precipitation value in the presence of the relatively strongly adsorbed hydrogen ion is similar to that in the presence of lithium ion and greater than that in the presence of either sodium or potassium ion.

¹¹ *J. Phys. Chem.*, **28**, 313, 457, 1029 (1924); **29**, 435, 517, 659 (1925); *Kolloid-Z.*, **34**, 262 (1924); **36**, 129 (1925); *Z. anorg. Chem.*, **142**, 345 (1925). See also Mukherjee and Ghosh, *Quart. J. Indian Chem. Soc.*, **1**, 213 (1924).

¹² Weiser, *J. Phys. Chem.*, **30**, 29 (1926).

Another explanation suggests itself: For a given alkali chloride concentration, precipitation will take place when the combined adsorption of the two cations neutralizes the combined adsorption of chloride and hydrosulfide ions. The combined adsorption will be equivalent for different pairs of cations; but the relative amounts of each that make up this equivalent adsorption will vary, depending as it does on the relative adsorbability of the two cations. If one may disregard for the moment the slight variation in the amounts of chloride added with barium chloride as compared with the relatively large amount of this

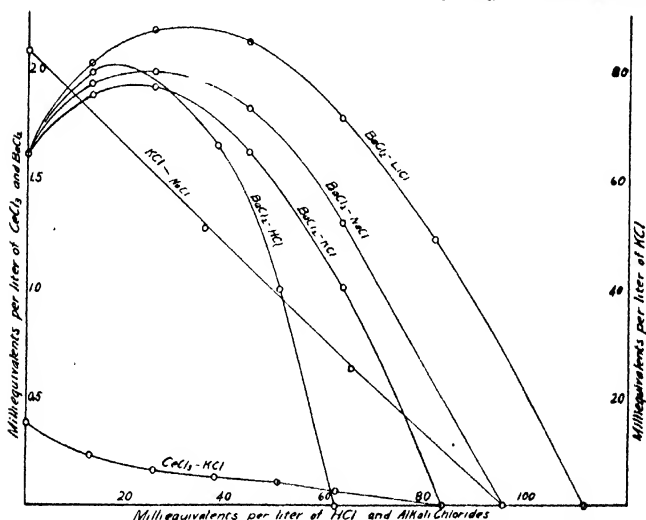


FIG. 1.—Precipitation of Arsenous Sulfide Sol with Mixtures of Electrolytes.

ion added with the alkali chloride, it follows that, for a given concentration of different alkali chlorides, the varying amounts of barium that must be added will depend on the effect of each cation on the adsorption of the other. Thus the adsorption of barium is cut down by lithium ion less than by potassium ion, tending to make the precipitation concentration of barium chloride less in the presence of lithium chloride than of potassium chloride. Hand in hand with this is the decrease in the adsorption of alkali by the presence of barium, which will tend to make the precipitation concentration of barium chloride higher in the presence of lithium. From this point of view, the latter factor appears to predominate with the alkali chlorides. With hydrochloric acid, however, the cutting down of the adsorption of barium by hydrogen ion is the

determining factor with lower concentration of hydrochloric acid while with higher concentrations of acid the second factor appears to predominate.

Another method of attack is to determine whether the presence of relatively small amounts of potassium chloride, say, increases the precipitation value for arsenious sulfide sol, of chlorides other than barium chloride. Observations with mixtures of potassium chloride with sodium chloride and cerium chloride respectively are given in Table VI and plotted in Figure 1.

TABLE VI
PRECIPITATION OF As_2S_3 SOL BY MIXTURES

KCl	+	NaCl	KCl	+	CeCl ₃
0.0		95.0	0.0		0.388
25.0		64.0	12.5		0.230
50.0		35.0	25.0		0.162
83.0		0.0	37.5		0.132
			50.0		0.105
			62.5		0.067
			83.0		0.000

The results are quite conclusive that the addition of potassium chloride does not increase the stability of arsenious sulfide sol toward all other chlorides. Thus the relationship is approximately additive with sodium chloride whereas the precipitation value of cerium chloride is decreased unmistakably by the presence of potassium chloride. It hardly seems probable that the latter result would obtain if potassium chloride in small concentration actually stabilized the sol in the same way that a highly purified ferric oxide sol is stabilized by the addition of a small amount of hydrogen ion or ferrocyanide sols by a small amount of ferrocyanide. In the absence of marked ionic antagonism between ions of the same sign, one might expect the precipitation values of mixtures to fall below the additive value on account of the relatively greater adsorbability of the precipitating ions at low concentration. This was actually observed in a number of instances with hydrous oxide sols.¹³ To account for the difference in the results with barium chloride and cerium chloride one should expect to find the adsorption of barium cut down much more strongly than cerium by the presence of proportionate amounts of potassium chloride. That such is the case is shown by the results recorded in Table VII on the adsorption of barium and of cerium, respectively, in the presence of 50 times the concentration of potassium chloride. Cerium was determined by the colorimetric method of Benz previously used successfully by Freundlich¹⁴ in measuring the adsorption of this element by arsenious sulfide. It will be

¹³ Weiser, *J. Phys. Chem.*, **28**, 232 (1924)

¹⁴ *Z. physik. Chem.*, **37**, 407 (1910).

TABLE VII

Solutions Mixed with 100 cc. Sol		N/200 CeCl ₃ Remaining		Ce Adsorbed Millieq. per Gram
Total Volume 200 cc.		cc		
N/200 CeCl ₃	N/2 KCl			
20	0	5.4		0.073
20	5	9.0		0.058
N/50 BaCl ₂	N/2 KCl	BaSO ₄ Remaining in 180 cc.		Ba Adsorbed Millieq. per Gram
30	0	0.0537	0.0537	0.064
30	30	0.0614	0.0615	0.010

noted that, under similar conditions, the adsorption of cerium is cut down less than 25 per cent, while the adsorption of barium is cut down almost 85 per cent.

Finally, the presence of potassium chloride does not raise the precipitation concentration of sodium chloride above the additive value as would be expected if the sol were stabilized appreciably by preferential adsorption of chloride ion. The precipitation values of such mixtures having a common anion, are additive since the adsorption of the precipitating cations are similar and so the adsorption of each is affected but slightly by the presence of the other within the limits of the precipitation concentration. On the other hand, with mixtures having precipitating cations in common and different anions, one should expect variations from additive values in proportion to the difference in adsorbability of the anions. Thus, I have found the precipitation concentrations for mixtures of potassium and sodium ferrocyanide to be additive whereas the critical concentrations for mixtures of potassium chloride and ferrocyanide rise slightly above the additive values,¹⁶ because of the greater adsorbability of ferrocyanide ion than of chloride ion.

That the stabilizing action of adsorbed chloride ion is probably not the most important factor in increasing the precipitation value of mixtures above the additive relationship is further emphasized by the agglomerating action of relatively low concentrations of alkali chloride. An arsenious sulfide sol was prepared according to the method of Freundlich and Nathanson.¹⁶ This sol when viewed in the ultramicroscope, gives a light cone but is practically free from ultramicros. The addition of small amounts of NaCl causes some agglomeration of the particles as evidenced by the appearance of ultramicros on standing. This phenomenon was investigated carefully in the following way: A quantity of the sol was prepared and filtered through an ultrafilter which removed any ultramicros that might be present. The preparation gave a clear uniform light cone. Ten cubic-centimeter samples of

¹⁶ Cf. Sen, *J. Phys. Chem.*, **29**, 517 (1925).

¹⁷ *Kolloid-Z.*, **28**, 258 (1921).

the sol were taken and diluted to 20 cc. with ultrafiltered water to which was added 0, 0.2, 0.5, and 0.7 cubic centimeters, respectively, of ultrafiltered N sodium chloride. Special care was taken in the cleaning of all apparatus with ultrafiltered water and in protecting the samples from dust. After standing for two hours, the samples were placed in the

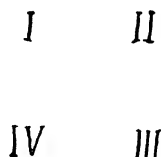


FIG. 2.

Biltz cell of a Zeiss slit ultramicroscope supplied with a camera, and the light cone photographed. The time of exposure was 2 minutes. A comparison of the photographs obtained (Figure 2) indicates agglomeration of particles in the presence of relatively small amounts of NaCl as evidenced by the gradually increasing intensity of the light cone in going from sample 1 containing no sodium chloride to sample 4 containing 0.7 cc. of N salt.

For the sake of comparison, the precipitation value curve of mixtures

of BaCl_2 and NaCl for the sol is given in Figure 3. The precipitation values were determined as described elsewhere,¹⁷ observations for complete precipitation being made after two hours. The ultramicroscopic observations referred to above were made on the pure sol and on samples containing 10, 25, and 35 milliequivalents of NaCl per liter, respectively. In this region the precipitation value of BaCl_2 is increased appreciably by the presence of sodium chloride although the agglomeration of the particles by the latter is clearly indicative of a decrease in the stability of the sol. It would seem, therefore, that in this case, cationic antagonism rather than the stabilizing action of the

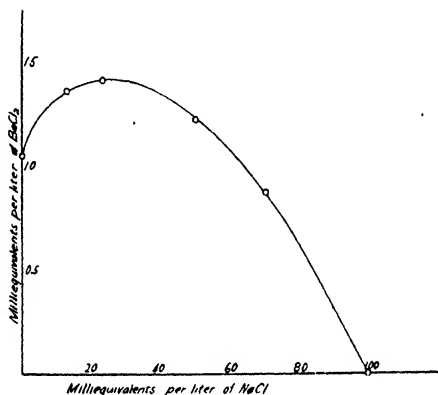


FIG. 3.—Precipitation of Arsenious Sulfide with Mixtures of BaCl_2 and NaCl .

anion is the most important factor in bringing about the variation from an additive relationship.

Ionic antagonism such as that between alkali and alkaline earth cations in the precipitation of arsenious sulfide sol has been recognized recently by other investigators. Thus Mann¹⁸ finds that NH_4Cl , MgCl_2 , and AlCl_3 cut down the adsorption of methylene blue and neutral red by discs of mangold root, the magnitude of the reduction being a function of the valency and concentration of the cation. The adsorption of both dye and salt attain equilibrium at a lower point than would be reached by either in the absence of the other, indicating mutual hindrance. And Dhar and his collaborators who have in several papers ignored or opposed the concept of antagonism between ions of the same charge, have finally embraced this view.¹⁹ "As is known, crystal violet

¹⁷ *J. Phys. Chem.*, **28**, 238 (1924).

¹⁸ *Ann. Bot.*, **38**, 753 (1924).

¹⁹ Ghosh, Bhattacharya, and Dhar, *Kolloid-Z.*, **38**, 145 (1926).

and strychnine hydrochloride cations are more strongly adsorbed by arsenious sulfide than barium and aluminum ions. On this account, the presence of the dye cations cut down the adsorption of K^+ , Ba^{++} , and Al^{+++} ions and therefore more than the calculated amount of KCl , $BaCl_2$, and $Al(NO_3)_3$ is required for the precipitation of the sol. On the other hand, in precipitating arsenious sulfide sol with mixtures of strychnine chloride and crystal violet, the values are practically additive since the cations of both substances are about equally adsorbed and, at the precipitation concentration, there is no antagonistic effect on the adsorption."

Although in certain cases the antagonistic action between precipitating ions may be the most important factor in determining the precipitation values of salt pairs, in other instances the effect of stabilizing ions may predominate. Thus Sen working with copper ferrocyanide sol, observed an increase in precipitation value of potassium chloride and of barium chloride in the presence of potassium ferrocyanide. With mixtures of potassium chloride and potassium ferrocyanide it is quite obvious that cationic antagonism cannot come in since both precipitating cations are the same. Mukherjee and Ghosh²⁰ observed a similar behavior with mixtures of sodium benzoate and sodium chloride on arsenious sulfide sol and I have already called attention to observations with potassium ferrocyanide and potassium chloride on the same sol. The determining factor in the latter cases is the stabilizing action of the relatively strongly adsorbed benzoate and ferrocyanide, respectively.

Consider the case of Graham's ferric oxide sol which owes its stability to preferential adsorption of hydrogen ion derived from hydrolysis of ferric chloride. It is too well known to need comment, that the stability of the sol falls off as the hydrogen ion concentration is decreased by dialysis and if the dialysis is continued long enough, all of the sol will precipitate. Conversely, if we add hydrochloric acid to a highly purified sol, the stability toward all electrolytes will increase. Similar stabilization would be expected on adding ferric chloride, aluminum chloride, or lanthanum nitrate, as Freundlich and Wosnesensky²¹ have shown. With the relatively insoluble Pean de St. Gilles sol, a maximum in the stability is reached on adding hydrochloric acid; and at a suitable concentration, the adsorption of the precipitating chloride ion neutralizes the adsorption of hydrogen ion and precipitation takes place.²² Similarly, colloidal copper ferrocyanide and Prussian blue are stabilized by preferential adsorption of ferrocyanide ion. The lower the concentration of the ferrocyanide ion the less the stability. On adding potassium ferrocyanide to a highly purified ferrocyanide

²⁰ *J. Indian Chem. Soc.*, **1**, 213 (1924).

²¹ *Kolloid-Z.*, **33**, 222 (1923).

²² *Weiser, J. Phys. Chem.*, **25**, 665 (1921).

sol, the stability toward all electrolytes should be increased until the concentration is high enough for the adsorption of the precipitating potassium ion to decrease the stability of the sol below the critical value. This is exactly what Sen observed with two electrolytes of widely varying precipitating power. The precipitation value of both potassium chloride and barium chloride is increased to a maximum that lies above the value for either electrolyte alone.²³

A survey of the data obtained by Sen indicates that the form of the precipitation value curve of salt pairs for negative colloidal copper ferrocyanide sol depends on whether cationic antagonism may come in or whether it is eliminated by using salt pairs with a common cation. Thus when precipitation concentration of potassium ferrocyanide as abscissa is plotted against that of potassium chloride as ordinate, the curve rises sharply to a maximum, bends sharply, and then follows an almost straight course to the precipitation value of pure potassium ferrocyanide. On the other hand with concentrations of barium chloride as ordinate the curve rises gradually to a broad maximum dropping sharply when near the precipitation value of pure potassium ferrocyanide. The difference between these curves obtained with copper ferrocyanide sol, and between either of them and curves obtained with arsenious sulfide sol, called for further investigation. Furthermore, certain discrepancies exist in the data. Thus Sen finds the precipitation values of KCl and $K_4Fe(CN)_6$ to be 40 and 140, respectively, for one copper ferrocyanide sol and for another similar sol, the values to be 35.6 and 260, respectively. Moreover, difficulty was encountered in determining the exact precipitation values because of reported slowness in settling of the ferrocyanide sol.

Colloidal copper ferrocyanide was prepared by precipitating dilute solutions of cupric chloride with a very slight excess of copper ferrocyanide. The precipitate was washed thoroughly by means of the centrifuge until it was carried into colloidal solution from which it could not be thrown down by centrifuging for ten minutes in a No. 1 International centrifuge making 3000 r.p.m. The sol thus formed was subjected to dialysis for three weeks, changing the water continuously in a Neidde dialyzer. Prepared in this way, the sol is quite pure as evidenced by the relatively low precipitation value of salts.

Since the finely divided precipitate obtained with univalent precipitating ions does not settle readily, the following procedure was used to obtain accurate precipitation values: Ten cubic centimeters of sol were mixed with a definite amount of electrolyte diluted to 10 cc. The mixture was allowed to stand two hours, after which 10 cc. of the supernatant liquid in the region of the precipitation value was withdrawn and centrifuged for 10 minutes at 3000 r.p.m. The supernatant

²³ *J. Phys. Chem.*, **29**, 517, 539 (1925), Sen and Mehrotra, *Z. anorg. Chem.*, **142**, 345 (1925).

liquid after centrifuging was transferred to a Nessler tube and examined for completeness of precipitation. With the exception of being rather time consuming, the procedure was entirely satisfactory. After getting the approximate precipitation values in a given series of experiments, the final, accurate values were obtained within 48 hours. The results with mixtures of potassium ferrocyanide and both potassium chloride and barium chloride are given in Table VIII and shown graphically in Figure 4.

TABLE VIII

PRECIPITATION OF COLLOIDAL $\text{Cu}_2\text{Fe}(\text{CN})_6$ BY MIXTURES (a)
(Precipitation values in milliequivalents per liter.)

$\text{K}_4\text{Fe}(\text{CN})_6$	BaCl_2	$\text{K}_4\text{Fe}(\text{CN})_6$	KCl
0.0	1.58	0.0	23.8
12.5	1.90	12.5	157.5
25.0	2.00	25.0	155.0
50.0	2.10	50.0	140.0
100.0	2.00	100.0	112.5
150.0	1.60	150.0	82.5
260.0	0.0	262.5	0.0

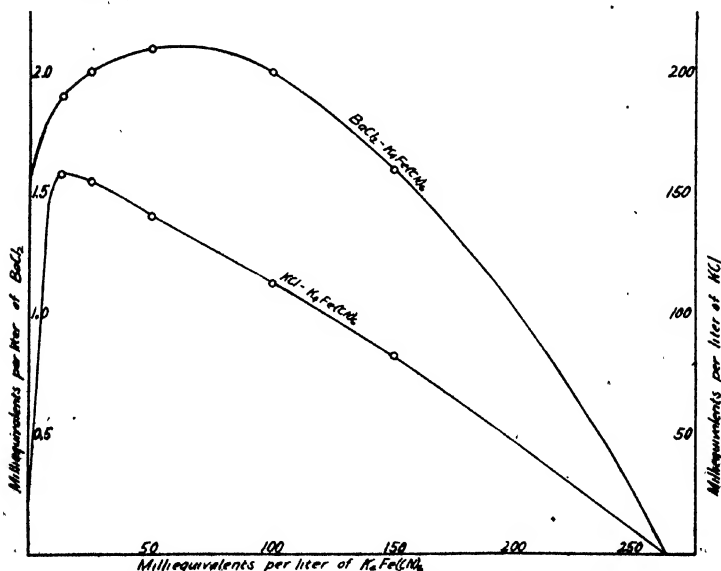


FIG. 4.—Precipitation of Copper Ferrocyanide Sol by Mixtures of Electrolytes (a).

It will be seen that the addition of potassium ferrocyanide causes the precipitation value of potassium chloride to mount sharply to a

value more than 6 times that of pure chloride. This indicates that the purity of the original sol with respect to ferrocyanide ion is much greater than that of Sen's sol. After the maximum is reached, the curve bends sharply and then follows an almost linear course as Sen also observed. This means that if one takes an impure copper ferrocyanide sol the precipitation values of mixtures of potassium ferrocyanide and chloride will be approximately additive on account of the absence of cationic antagonism. A similar type of curve should result with mixtures of barium ferrocyanide and barium chloride. This was found to be true so far as the linear part of the curve is concerned; but the sharp maximum could not be detected with certainty since the precipitation concentrations of the chloride and ferrocyanide of barium were so close together.

On turning to the potassium ferrocyanide-barium chloride curve, contrary to Sen's observations, one is impressed with the very great similarity to the curves obtained with alkali-alkaline earth salt pairs on arsenious sulfide sol. Since in the latter case both cationic antagonism and the stabilizing action of the anion play a rôle, it is possible that the difference between the potassium ferrocyanide-barium chloride curve and the potassium ferrocyanide-potassium chloride curve with copper ferrocyanide sol, is due to the absence of cationic antagonism in the first instance and its presence in the second.

It should be emphasized however that the initial increase in precipitation value of BaCl_2 in the presence of potassium ferrocyanide is due primarily to the effect of ferrocyanide ion. Thus from the results recorded in Table IX and shown graphically in Figure 5, it will be seen that the precipitation values of mixtures of KCl and BaCl_2 fall

TABLE IX
PRECIPITATION OF COLLOIDAL $\text{Cu}_2\text{Fe}(\text{CN})_6$ BY MIXTURES (b)
(Precipitation values in milliequivalents per liter.)

KCl	+	BaCl_2	KCl	+	CuCl_2
0.0		1.58	0.0		0.350
2.5		1.38	2.5		0.275
5.0		1.26	5.0		0.265
10.0		0.97	7.5		0.245
12.5		0.83	11.8		0.180
13.8		0.75	16.8		0.100
20.0		0.25	23.8		0.000
23.8		0.0			

slightly below the additive value at the lower concentrations of KCl; but at higher concentrations of KCl the values are slightly greater than additive. The same is true for mixtures of KCl and CuCl_2 and of KCl and CuSO_4 .²⁴ For arsenious sulfide sol, the cationic antagonism

²⁴ Cf. however, Gurchot, *J. Phys. Chem.*, 30, 98 (1926).

between potassium and barium ion is greater in ferrocyanide than in chloride solution.²⁵ No experiments have been carried out to determine whether a similar condition exists with copper ferrocyanide sol.

As a result of these observations, it is evident that the precipitation values for sols of mixtures of two electrolytes may be additive, may be greater than the additive values, or may be less than the additive values. Moreover, it would seem that three factors, at least, may influence the precipitation concentration of salt pairs: (1) The effect of each precipitating ion on the adsorption of the other, (2) the stabilizing action of ions having the same charge as the sol, and (3) the relatively greater adsorbability of ions at lower concentrations. The antagonistic action between precipitating ions of the same charge is important in

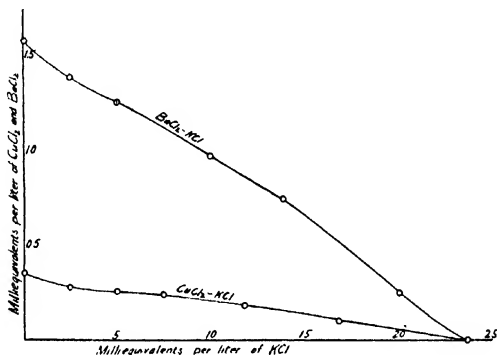


FIG. 5.—Precipitation of Copper Ferrocyanide Sol by Mixture of Electrolytes (b)

raising the critical concentrations above the additive value only in cases where the ions show a marked difference in adsorbability. Variation from the additive relationship with mixtures of salt pairs having a common precipitating ion, results only when there is an appreciable difference in the adsorbability of the stabilizing ions, the magnitude of the variation from an additive relationship being determined by the difference in adsorbability. If the first and second factors referred to above are not too pronounced, the precipitation values of mixtures may fall below the additive value on account of the relatively greater adsorbability of precipitating ions at low concentration.

Since the addition of alkali chloride to arsenious sulfide sol and to alkali ferrocyanide to copper ferrocyanide sol increases the precipitation value of BaCl_2 , the question arises whether the sols coagulated by BaCl_2 alone will be reprecipitated by the addition of alkali salt. The

²⁵ Weiser, *J. Phys. Chem.*, 30, 29 (1926).

answer is, that it will be provided the alkali salt exerts an appreciable peptizing action. When a sol like Freundlich and Nathanson's arsenious sulfide is treated with barium chloride, the very minute primary colloidal particles coalesce into larger primary ultramicros which finally agglomerate into secondary particles and these, in turn, into clumps. If potassium chloride is added to such a coagulum a sol is not reformed on account of the relatively low peptizing action of chloride ion. On the other hand, the addition of potassium ferrocyanide to a copper ferrocyanide coagulum reverses the coagulation on account of the marked peptizing power of the anion for copper ferrocyanide.

Attention should be called, in passing, to an interesting property of arsenious sulfide. It has been observed repeatedly that the critical concentration of electrolytes does not cause agglomeration of the neutralized particles into a clump, unless the mixture is shaken. What apparently happens is, that the charge on the particles is neutralized, but instead of agglomerating into a clump the individual particles with their film of adsorbed water coalesce to a loose jelly structure that is broken up by shaking. If a concentration of electrolyte close to the critical value is used and the sol is allowed to stand quietly for a day or two, the surface of the precipitate as it settles, appears to be a fairly strong, translucent, mobile film strikingly similar in appearance to that of a copper ferrocyanide membrane.

III. Ionic Antagonism in Biological Systems.

The behavior of colloidal solutions of such substances as arsenious sulfide and copper ferrocyanide in the presence of salt pairs is of importance owing to the existence of what appear to be analogous phenomena in biological systems.

Forty-five years ago, Ringer²⁶ attempted to use a sodium chloride solution isotonic with the blood, for the continuous perfusion of the heart of a frog. This solution was unsatisfactory as the beats diminished gradually and ceased entirely after a few minutes. It was discovered that traces of the chlorides of calcium and potassium added to the salt solution gave a perfusion liquid capable of maintaining the heart beat at a satisfactory height for a considerable time. The so-called "Ringer's solution" contains 0.13 M NaCl, 0.0011 M CaCl_2 , and about 0.0002 M KCl.²⁷ Similarly, Jacques Loeb²⁸ found that certain marine organisms are killed quickly when transferred to a solution of sodium chloride having the same concentration as sea water; but the destructive action of the sodium chloride is neutralized by adding CaCl_2 in the ratio of one or two mols of the latter to 200 of the former. It is a striking

²⁶ *J. Physiol.*, **3**, 380 (1880-82); **4**, 29, 222 (1882-83); **7**, 291 (1886).

²⁷ Bayliss, "Principles of General Physiology," 207 (1920).

²⁸ *Pflüger's Arch.*, **97**, 894 (1903); Loeb and Wasteneys, *Biochem. Z.*, **32**, 308 (1911); *J. Biol. Chem.*, **21**, 223 (1915).

fact that the optimum ratio of NaCl to CaCl_2 is approximately the same as it is in nature, in sea-water, and in the blood of animals. A similar relationship obtains with certain plants. Thus Osterhout²⁹ demonstrated that wheat grown in a solution containing 0.12 M NaCl and 0.0012 M CaCl_2 develops extensive rootlets and shows other signs of healthy growth whereas in solutions of either 0.12 M NaCl or 0.0012 M CaCl_2 alone, no growth occurs. Moreover, zoospores of *Vaucheria* grow rapidly in a solution of 0.01 M NaCl and 0.0001 M CaCl_2 or even in pure water; but show no signs of growth in either 0.01 M NaCl or 0.0001 M CaCl_2 . Observations of a similar character have been made repeatedly by a number of other biologists³⁰ so that the antagonistic action of salts on living organisms can be considered as one of the commonplaces of biological science.

The influence of salts on living cells appears to be closely related to their permeability. Osterhout³¹ studied the effect of various electrolytes on the conductivity of certain sea weeds such as *Laminaria*. Immediately after removal from sea water he found the tissues to exhibit a practically constant resistance to the passage of the current; but on exposure to a comparable NaCl solution the resistance decreased and to a comparable CaCl_2 solution the resistance increased; while exposure to properly balanced mixtures containing 100 mols NaCl to 1 to 2 mols CaCl_2 caused no appreciable variation from the normal. If *Laminaria* is first immersed in a 2.5 per cent solution of pure sodium chloride the electrical conductivity is increased; on adding a little calcium chloride to the solution, the sea weed returns to normal conductivity without showing signs of permanent damage.³² It appears, therefore, that the protoplasmic membrane is a physical system capable of undergoing reversible variations in permeability as a result of exposure to solutions containing varying amounts of sodium and calcium salts. From such observations, Osterhout³³ divides substances into two groups (1) those which cause an increase in permeability and (2) those which can produce a decrease in permeability. From this point of view, substances belonging to the first class will antagonize those belonging to the second and vice versa. "The soundness of this point of view is indicated not only by the fact that we are able to predict both qualitatively and (to a considerable extent) quantitatively the effect of combinations of salts but also by the very significant fact that we are able to extend this conception to organic compounds and to show that non-electrolytes which decrease permeability can also antagonize such substances, as

²⁹ *Plant World*, 16, 129 (1913); *J. Biol. Chem.*, 19, 335 (1914).

³⁰ Cf. Lillie, *Am. J. Physiol.*, 29, 372 (1912); Netter, Höber's "Physik. Chem. d. Zelle u. d. Gewebe," Part II, 662, 668; Spirc, *Schweiz. med. Wochenschr.*, 51, 457 (1922); Utin, *Chem. Zentr.*, III, 887 (1922).

³¹ *Science* (2), 35, 112; 36, 350 (1912).

³² Osterhout, *Science* (2), 34, 187 (1911).

³³ *Science* (2), 41, 266 (1915).

NaCl. These facts indicate that the hypothesis may be applied in a general manner so as to include both electrolytes and non-electrolytes."

This hypothesis does not account for the change in permeability, but Clowes³⁴ has sought to explain it by comparing the cell membrane to an oil-water emulsion in which soaps concentrate at the interface between oil and water lowering the surface of one or the other depending on whether the soap is oil-soluble or water-soluble.³⁵ Thus we should expect an emulsion of oil in water in the presence of sodium salts and of water in oil in the presence of calcium salts. "Salts of calcium promote and alkalis and salts of sodium inhibit the transformation of a system consisting of a non-aqueous phase dispersed in water into the reverse type of system, consisting of water more or less perfectly dispersed in a non-aqueous phase. If the analog of islands surrounded by water and lakes surrounded by land is considered, it will be obvious that a transformation has been effected from a system which is freely permeable to water to one which is impermeable, if the transformation is complete. Since the transformation in one direction is effected by salts of calcium and in the reverse direction by salts of sodium, any intermediate degree of permeability might well be obtainable by simply varying the proportions of the salts of sodium and calcium introduced into the system." From this point of view, it would follow that the critical ratio of sodium and calcium salts is one which produces a balance between the two types of emulsion that is most favorable for life and growth. In support of his hypothesis Clowes, working with oil, water, and soap, showed that the ratio of sodium and calcium salts necessary to produce a balancing between these two types of emulsions was about the same as that found in sea water. Although quite suggestive, Clowes' view that a cell membrane is a labile emulsion is inadequate to account for the marked osmotic pressure which a cell manifests. It seems better, at least for the present, to consider the cell membrane as a more or less rigid, semi-permeable pellicle comparable in certain respects to a copper ferrocyanide membrane.

From what we now know of the structure of jellies and gelatinous precipitates,³⁶ it seems probable that a copper ferrocyanide membrane consists of myriads of minute particles which adsorb water strongly. As a result of investigations carried out in Bancroft's laboratory Gurchot³⁷ considers a copper ferrocyanide film to be a negative colloidal film analogous to a colloidal sol. It is therefore a granular membrane the space between the particles of which is more or less completely filled with adsorbed water. The film is therefore a dynamic system capable of reversible coagulation.

³⁴ *J. Phys. Chem.*, 20, 407 (1916).

³⁵ Bancroft, "Applied Colloid Chemistry," 261 (1921).

³⁶ Cf. Weiser, Bogue's "Colloidal Behavior," 1, 377 (1924).

³⁷ *J. Phys. Chem.*, 30, 83 (1926).

This concept of the nature of a copper ferrocyanide membrane enables one to account for a number of facts. To illustrate, it is known that below a certain concentration of salts the latter will pass through a copper ferrocyanide membrane and sugar will not; while at higher salt concentrations, both will pass through. This is explained by assuming that no coagulation of the membrane takes place below a certain critical concentration of salt. The salts being soluble in water dissolve in the water layer and so pass through the membrane. Sugar molecules cannot go through in this way because of strong negative adsorption. When the salt concentration reaches the critical coagulation value, there results agglomeration of the particles which carry with them their film of adsorbed water leaving cracks through which the sugar can pass. Reversing the coagulation by adding a peptizing agent reforms the semipermeable film and the sugar will no longer pass through. Gurchot apparently succeeded in accomplishing this reversal in permeability to sugar after coagulation with alcohol and salts, by means of CuSO_4 . For some reason Gurchot did not try potassium ferrocyanide which would doubtless have produced the desired results in very low concentration. The difficulty of testing for sugar in the presence of ferrocyanide does not seem to be sufficient reason for not trying the latter reagent.

If the membrane of a living cell is a colloidal film similar to a colloidal sol that can undergo reversible coagulation, there would appear to be a close analogy between the action of salt pairs in the precipitation of such sols as copper ferrocyanide and arsenious sulfide and the antagonistic action of salt pairs on the permeability and hence on the life and growth of living cells. From this point of view, all of the factors influencing the precipitating action of salt pairs as it effects the stability of sols, which I have outlined above, will be concerned in the antagonistic action of salt pairs as it affects the permeability of protoplasm.

Summary.

1. In the precipitation of sols there is an antagonistic action between the oppositely charged ions of a precipitating electrolyte in the sense that the greater the adsorption of the stabilizing ion, the greater must be the adsorption of the precipitating ion to effect neutralization.

2. In the simultaneous adsorption from mixtures of two electrolytes having no ion in common, the most readily adsorbed cation and anion are taken up most and the other pair least readily; while from mixtures having one ion in common, the oppositely charged ions are each adsorbed less than if the other were absent but the most readily adsorbed ion is displaced the least.

3. The precipitation values for sols of mixtures of two electrolytes may be additive, may be greater than the additive values or may be less than the additive values.

4. The factors which determine the precipitation concentration of mixtures are: (1) The effect of each precipitating ion on the adsorption of the other. (2) The stabilizing action of ions having the same charge as the sol. (3) The relatively greater adsorbability of ions at lower concentrations.

5. The antagonistic action between precipitating ions of the same charge is important in raising the critical concentrations above the additive value, only in case the ions show a marked difference in adsorbability. This effect predominates when arsenious sulfide sol is precipitated by mixtures of the chlorides of barium and potassium.

6. Under certain conditions, the critical values for mixtures of two electrolytes may rise above the additive value even when the precipitating ions of the two are identical, thus eliminating antagonism between precipitating ions.

7. Variation from the additive relationship with mixtures of salt pairs having a common precipitating ion, results only when there is an appreciable difference in the adsorbability of the stabilizing ions, the magnitude of the variation from an additive relationship being determined by this difference in adsorbability.

8. If the first and second factors referred to in (4) are not too pronounced, the precipitation values of mixtures may fall below the additive value on account of the relatively greater adsorbability of precipitating ions at low concentrations.

9. The antagonistic action of salt pairs on protoplasm is determined by their effect on the permeability of the cell membrane.

10. The membrane of a living cell may be a colloidal film similar to a colloidal sol that can undergo reversible coagulation. If so, there would appear to be a close analogy between the action of salt pairs toward such sols as copper ferrocyanide and arsenious sulfide and the antagonistic action of salt pairs on the permeability and hence on the life and growth of living cells.

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